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SAMPLING STRATEGIES FOR ESTIMATING THE MAGNITUDE AND IMPORTANCE OF INTERNAL PHOSPHORUS SUPPLIES IN LAKES

By

Robert E. Stauffer
Water Chemistry Laboratory
University of Wisconsin
Madison, Wisconsin 53706

Project Officer

Spencer A. Peterson
Freshwater Division
Corvallis Environmental Research Laboratory
U.S. Environmental Protection Agency
Corvallis, Oregon 97330

CORVALLIS ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CORVALLIS, OREGON 97330

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ABSTRACT

The physical and chemical factors controlling sediment release and water column cycling of phosphorus and other nutrients (internal loading) are discussed within a "systems" framework. Applying the systems approach, time-dependent nutrient storage within identified compartments, and fluxes between compartments are identified and interpreted mechanistically. The lake "system" is partitioned into four main compartments, the lake water, atmosphere, tributary land drainage, and underlying sediments. The lake water and adjacent sediments are further partitioned along the vertical axis to reflect seasonal thermal stratification, and sedimentation processes. The important mechanistic paradigms applied to the "system" include transport phenomena in density stratified fluids subjected to wind power, and the interacting geochemistries of iron, phosphorus, and sulfur in bicarbonate-buffered natural waters. The purpose of the model is to identify the chemical and morphological factors regulating phosphorus recycling in lakes, and lay a mechanistic foundation for a general model of the phosphorus "economy" of the epilimnion.

The magnitude and fate of sediment-released P into the overlying water column depends on the physical-chemical mechanism of release. In highly turbulent sediment interface environments of high redox potential, phosphorus release depends on the difference between the "cross over" concentration of the surficial sediment and the dissolved inorganic phosphorus concentration in the overlying water column. The "cross over" concentrations are typically much higher in calcareous than non-calcareous epilimnetic sediments, as a consequence of different edaphic conditions in their respective drainage basins. During summer, epilimnetic photosynthesis raises the pH and lowers the free water dissolved inorganic P concentration below the sediment "cross over" concentration: This condition promotes oxic sediment P release in calcareous lakes.

In the more general case of quiescent, or bio-turbated sediments, the magnitude and fate of sediment released P depends on the Fe/P stoichiometry of release. If the atomic Fe/P ratio exceeds 1.8, phosphorus is nearly quantitatively precipitated as ferric-phosphate when Fe^{2+} is oxidized by dissolved oxygen during diffusion upward through the overlying water column. As a consequence, phosphate released during stagnation into the anoxic bottom waters of deep non-calcareous lakes plays no subsequent role in the phosphorus economy of the trophogenic layer. However, in calcareous drainage lakes, low Fe/P release ratios <<1.0 typically occur because of selective sulfide inactivation of Fe(II) (as the precipitate, FeS) at the sediment-water interface. These alkaline lakes accumulate H_2S instead of Fe^{2+} in the anoxic hypolimnia, and hence, are called "sulfuretums". Calcareous lakes are prone to become sulfuretums because of low Fe weathering rates in the alkaline pervious soils of the drainage basin, the relatively high concentrations of sulfate in the hypolimnion available for reduction, and the high productivities and organic deposition rates for these lakes. Such lakes are efficient at recycling sediment-released P back into the trophogenic layer(s) because a chemical separation of Fe and P has occurred in the recycle pathway. In the absence of Fe, P is not naturally precipitated in the presence of oxygen. The purpose of alum treatments is to substitute aluminum inactivation of P in lakes lacking strong Fe regulation.

A methodological section discusses essentials of lake sampling, chemical analyses, estimation of vertical nutrient transport using flux gradient calculations, and interpretation of lake chemical budgets. A chronology of essential tasks is presented for the lake manager or scientific consultant interested in documenting internal cycling of nutrients in lakes.

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I. Introduction

During the past decade a number of case studies have established sediment phosphorus release (internal supply) as one important factor regulating the seasonal and annual trophic condition of a lake (Burns and Ross, 1972; Larsen *et al*., 1979; 1980; Cooke *et al*., 1977; Stauffer, 1974). Burns and Ross (1972) showed that pelagic sediment releases of P and hypolimnetic accumulation in Lake Erie's Central Basin resulted from prior onset of anoxic conditions at the sediment-water interface. This prior onset of anoxia also appeared to be a necessary condition for P release in Shagawa Lake, Minnesota (Larsen *et al*., 1979; 1980). However, Stauffer (1974) showed that, unlike lakes Erie or Shagawa, large scale P build-ups in the hypolimnion of Lake Mendota, Wisconsin *predate* the onset of anoxic conditions. Furthermore, Stauffer and Lee (1973) showed that P released into the hypolimnion of Lake Mendota could be transported through the summer thermocline during cold fronts in such magnitude as to be the dominant source of phosphorus to the epilimnion during the entire stratification period. Subsequent investigations (Stauffer, 1974) showed that large scale vertical transport of nutrients accompanying storms was also important in other calcareous drainage lakes of southern Wisconsin. Blanton (1973) and Sweers (1970) have also noted the potential for thermocline-migration-entrainment.

In the present paper I consider sampling strategies for estimating the magnitude and importance of internal phosphorus supplies in lakes. More specifically, I describe the following:

1. *What* physical and chemical measurements yield useful information about both the magnitude and fate of sediment phosphorus release? How analytically are these measurements made with the prerequisite precision and accuracy at the least cost?

2. *When* should the measurements be made, both from an annual perspective and within seasons? How are these decisions based on climatic factors, lake morphology, and the relation of the lake to its drainage basin?

3. *Where* on the lake surface do you sample? How do you take and process samples and (when necessary) preserve them for later analyses? How does the spatial arrangement of sampling stations depend on antecedent weather variables?

4. *How* do you process the data? In what ways can you use accumulating information to revise and refine the lake sampling and analytical strategies provided sufficient attention is paid to site-specific climatic influences on the seasonal stratification cycle.

Extensive physical-chemical data from lakes in the cold-temperate climate in the upper Midwest form the basis for the discussion of error analysis and optimal sampling strategies. However, based on accumulating evidence about underlying chemical principles and transport mechanisms, the results are likely to be broadly adaptable to lake investigations throughout the world. A brief section on climatic influences on physical limnology introduces some of these considerations. The *importance* of internal phosphorus supplies depends on both the long term and seasonal *balances* between the external supply and the internal, or recycled nutrient supply. Hence, this paper should be used in conjunction with Reckow's (1980) treatment of external sources for developing lake survey and management plans.

II. Lakes as Physical Chemical Systems

A. Compartments-Linkages

Following the initiative of Chemical Engineering, it is useful to think of a lake (the water), its adjoining sediments, and its upstream drainage basin as comprising a compartmentalized physical-chemical system. This system responds over the long term to the annual climatic cycle, and in the short term to specific weather events which represent statistical "noise" in the climatic cycle. The system components or compartments influence one another through linkages. The linkages are controlled by climate and weather. For our purposes we will be mainly concerned with time series interpretations of nutrient accumulation (and loss) within identified compartments and the flux rates between compartments.

B. Drainage Basin Fluxes

The most important influence on lake chemistry is the drainage basin. Over the long term lakes reflect drainage basin influences, just as we are "What we eat". Many seminal illustrations of this fact can be cited, going back especially to Mackereth's (1966) classic paper on the English Lake District. The drainage basin-lake relation is essentially a one-way linkage. The drainage basin receives precipitation, chemically transforms this precipitation during the rock and soil weathering process (c.f. Holland, 1978) and the exports the precipitation excess (the difference between precipitation and evapo-transpiration; c.f. Linsley *et al.*, 1958) either as groundwater seepage inflow (to the lake) or tributary inflow. The lake receives the water and its dissolved solutes as an irreversible (except by evaporation and reprecipitation) inflow down the hydraulic gradient. Because precipitation excess is an areal-dependent time series related to precipitation, air temperature, air humidity, and vegetative development in the watershed, the temporal importance of drainage basin solute export to the lake depends both on $(A_{db} - A_o)/A_o$ and the specific weather sequence. [Note: A_o is the lake's surface area; $A_{db} - A_o$ is the land drainage to the lake.] It follows that no interpretation of changes in lake nutrient storage can exclude, *a priori*, the assessed potential for drainage basin export of these nutrients. This is important in designing sampling strategies for estimating sediment nutrient release and its fate in the water column.

The concentrations of individual nutrients exported from the drainage basin depend sensitively and uniquely on the specific history of rock-soil-water relations following the precipitation event. Dissolved silica concentration is determined by relatively rapid adsorption-desorption reactions between the water and dominant clay minerals comprising drainage basin soils

(Kennedy, 1971; Siever and Woodford, 1973; Mayer and Gloss, 1980). Thus, direct rainwater and snow-melt run-off (off frozen ground) can be relatively impoverished in SiO_2. Otherwise, concentrations range mainly from 8 to 15 mg L^{-1} throughout most of the temperate zone over most of the year. Low concentrations are often indicative of silica sedimentation (removal) in an upstream lake or reservoir as silica is used in macro amounts as an essential nutrient for diatom growth.

Drainage basin export of inorganic nitrogen is mainly in the form of nitrate, as ammonia is oxidized microbiologically to NO_3 and ammonia is both effectively adsorbed by clay minerals and preferentially utilized by vegetation for growth. High dissolved ammonia concentrations represent local pollution (ammonification of sewage or manure) or direct fertilizer run-off. Nitrate is frequently highly enriched in surficial ground waters draining improved agricultural land because of the ion's high downward mobility in soils and heavy applications of inorganic nitrogen as fertilizer to agricultural soils.

Phosphorus is relatively enriched in soil solutions of rich fertilized agricultural topsoils (Schroeder, 1976). Low equilibrium concentrations are typical of less fertile subsoils and severely leached soils rich in Fe and Al. The analysis of soil "cross-over" or equilibrium concentration has been described by Mayer and Gloss (1980) and Schroeder (1976). Drainage basin export of potentially "biologically available phosphorus" (c.f. Oglesby and Schaffner, 1978; Schaffner and Oglesby, 1978) is encouraged by large scale erosion of surficial topsoil under low temperature conditions at a time when drainage basin vegetative utilization of phosphorus has been minimal. In the north temperate climates these conditions are best satisfied in the late winter and early spring.

The expected time series for drainage basin water export can be estimated by substracting potential evapo-transpiration from precipitation norms on a seasonal basis (Linsley et al., 1958). Seasonal accuracy is improved if precipitation falling as snow is "stored" until the thaw. Noting the above, and equating "potential evapo-transpiration" to estimates of Lake Mendota evaporative losses (Linsley et al., 1958, p. 118) during summer stratification (Stauffer, 1980a), drainage basin water export can be constructed for the "normal" year and for several recent years featuring observed departures from precipitation norms (Figures 1, 2). Improved estimates could be generated using carefully calibrated algorithms like the Stanford Watershed Model. Obviously, it is preferable to have actual gaged estimates of tributary inflow and actual solute concentration data (Cooke et al., 1977; Larsen et al., 1979); however, such information is expensive to collect in a "provisional" analysis of the lake system.

Examining Figures 1, 2, I note that expected drainage basin export of "excess precipitation" is important in Wisconsin in the late fall and especially in the later winter and early spring. In the "normal" year net export is only ~1 cm month^{-1} during May and June and then turns negative until mid-September. The summer is a period of accumulating soil-moisture deficit for Wisconsin watersheds. From Table 1 we can calculate that each 1 cm of drainage basin water export is equivalent to 1.19% of Lake Mendota's total

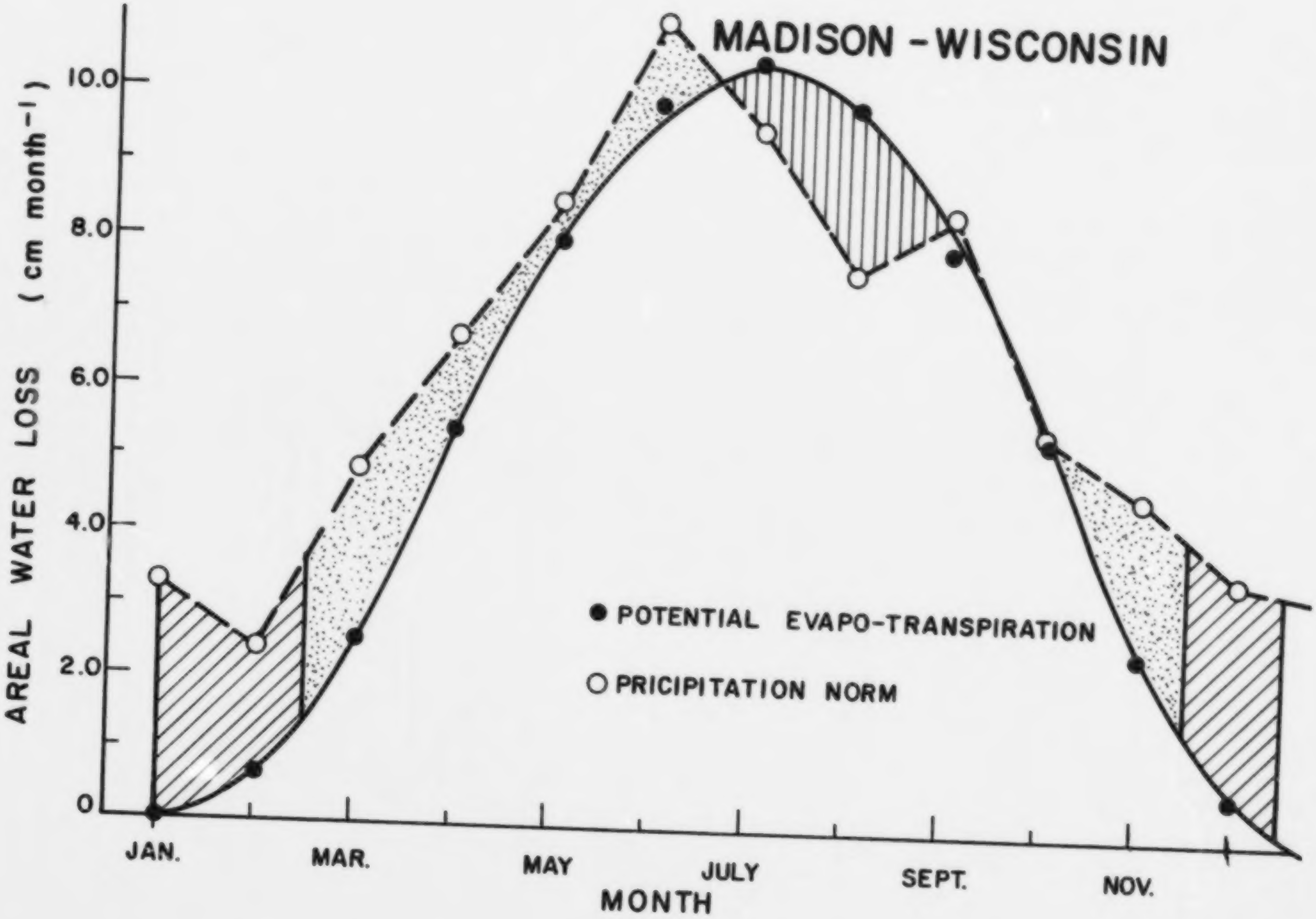

Figure 1. Monthly precipitation normals and potential evapo-transpiration for Madison, Wisconsin.

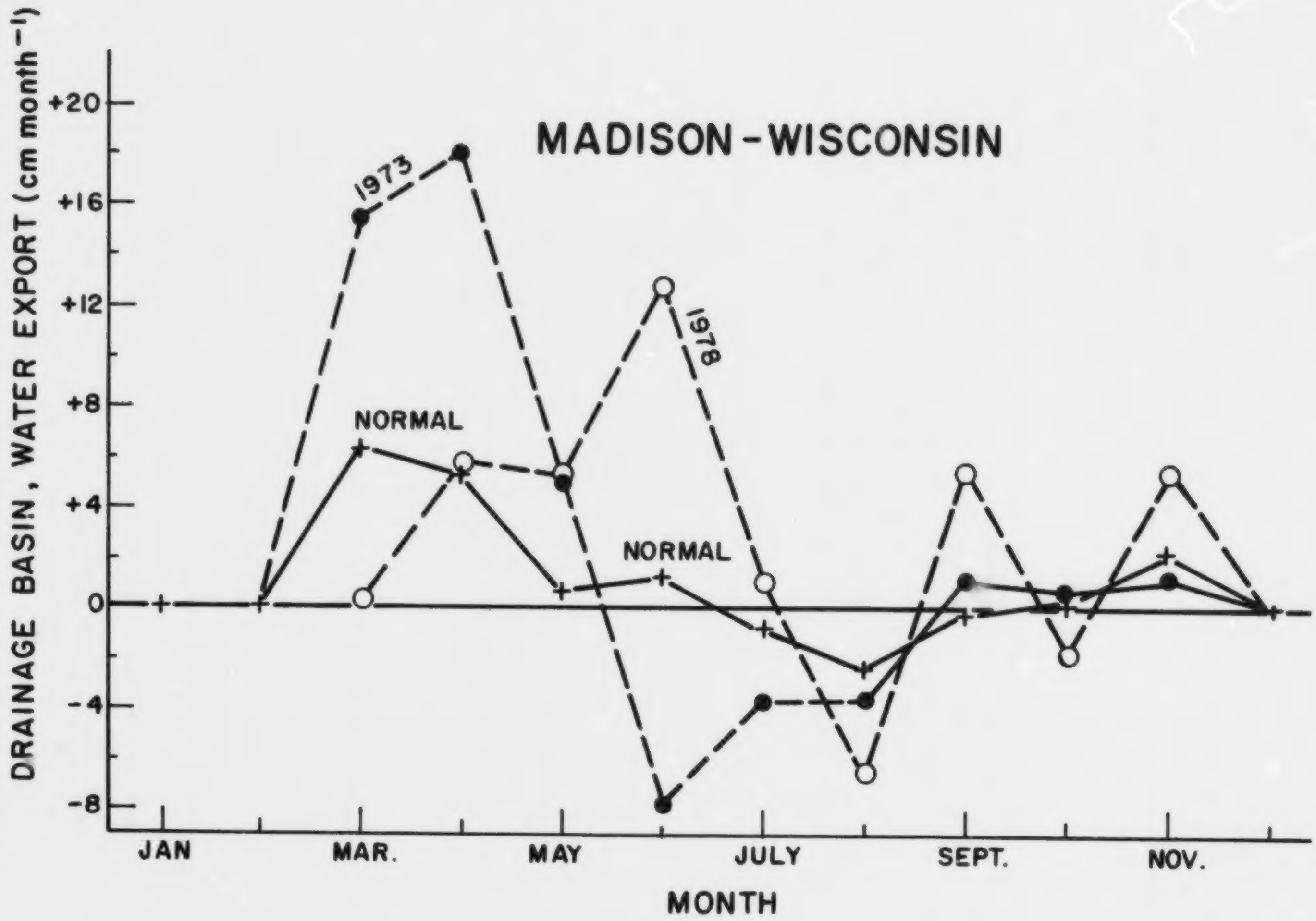

Figure 2. Drainage basin water export, Madison, Wisconsin. (Note: Precipitation December, January, February stored as snow; one-half is released in March; one-half in April.)

volume, and 2.20% of the epilimnion volume during typical mid-summer thermocline conditions. Noting that the total-P concentrations in the rural tributary waters of Lake Mendota (Lathrop, 1978) and Green Lake average ~40 mg m^{-3} during summer base-flow recessions (Stauffer, 1974; 1979, unpublished data), and that this is approximately the mean midsummer Mendota epilimnion concentration, it is clear that in the "normal" year net additions of P to the lake from the drainage basin during May-September are negligible. This also applies to Green Lake and Fish Lake. Conversely, in the early spring and late fall, total-P concentrations in the tributary waters both increase by an order of magnitude, and are associated with high discharge. Recent exhaustive monitoring studies of the Lake Mendota drainage basin (Lathrop, 1978) have confirmed this marked seasonality in drainage basin phosphorus loading.

Silica and NO_3-N exports from the drainage basin during May-September are quantitatively much more important than for P because of the very large Si/P and N/P ratios in the base flow recession stream waters (Stauffer, 1974). Additions of these nutrients are likely to be especially important during summer months with well above normal precipitation (note May-June 1978 in Figure 2). After entering the summer period of cumulative soil moisture deficit along with the concomitant emergence of vegetative cover, even heavy rains fail to mobilize much phosphorus in the pervious well-drained Wisconsin soils.

The above analysis shows that the incremental additions of P from the drainage basin can be ignored during thermal stratification unless the summer is so wet as to initiate erosion, and/or point sources of P (for example, municipal sewage) are important in the annual phosphorus budget. The seasonal pattern of external P loading also applies to erosion of clastics in the drainage basin. Because Fe is transported almost entirely as coatings on clay minerals (Carroll, 1958; Stauffer and Armstrong, 1980a) in alkaline drainage basins, the summer flux of Fe is also negligible in southern Wisconsin. Conversely, in arid climates with summer thunderstorm influences, external inputs of P and Fe accompanying clastics erosion can be maximum in the summer months (Gloss *et al.*, 1980). In mediterranean climates the summer flux falls to zero (Kennedy, 1971).

C. Time Dependent Density Partitioning of the Water Column

1. Introduction to Stratification: Convective Circulation.

Until now I have considered the lake water as one compartment in the tripartite: drainage basin-lake water-lake sediment chemical systems. However, treatment of the lake as an integral whole is appropriate only during those periods when it is isothermal and freely circulating. Because of the temperature-dependence of water density (c.f. Hutchinson, 1957) the addition or subtraction of heat at either the lake's atmospheric boundary or sediment benthic boundary acts to either induce or suppress water column circulation. We are thus led to the following important definition: The true mixed layer thickness or *free* convective circulation depth at any time t is denoted $h_c(t)$, and is that point in the water column (measured positively downward from the lake surface) above which $\Delta\rho/\Delta z \leq 0$ for all $z < h_c(t)$. Because pure water attains its maximum density at 4°C, once the lake cools below 4°C in the fall it resists mixing and is subject to winter stagnation. Winter stagnation is enhanced by ice cover because ice uncouples the lake from the forced circulation influences of the wind.

Adopting Hutchinson's (1957) descriptive terminology, temperate lakes of sufficient depth are either dimictic if they circulate in the fall and early spring, or monomictic if they circulate from the late fall through the early spring. Winter stagnation under ice persists in southern Wisconsin approximately from mid-December to mid-April. In northern Wisconsin, Minnesota, Michigan and New England the duration of ice cover is about one month longer. Because of their greater heat capacities, large deep lakes have delayed ice-on and ice-out dates.

2. Duration of Vernal Isothermal Convective Circulation

Following ice-out, and until the lake attains an average temperature of 4°C, net heat additions to the lake's upper layers by the direct absorption of solar radiation or sensible heat transfer (warm air overlying cold water) generate buoyancy instability and induce free convective circulation. These convections penetrate to the lake bottom unless the bottom benthic layer is significantly density stabilized by important accumulations of dissolved or suspended solids [such lakes are called "meromictic", c.f. Hutchinson, 1957; Judd, 1970; Walker, 1974, for example].

The duration of the vernal free convective circulation period depends sensitively on two factors: (1) the lake's mean depth ($\bar{z}$) and mean lake temperature ($\bar{T}_L$) at ice-out; hence the heat (cal cm^{-2} surface area) required to warm it to 4°C ($100\ (4-\bar{T}_L)*\bar{z}$); (2) the rate of lake heating following ice-out. Because large windswept lakes usually cool to 1 to 2°C prior to ice-on, large deep lakes require a long heating period to attain 4°C. Because most of the heating is accomplished by solar radiation, and insolation increases as we approach the summer solstice, the later the date of ice-out the shorter the expected duration of the vernal convective circulation period.

Assuming a mean lake temperature of 2°C at ice-out, and a lake heating efficiency of 70% (% of incident radiation including infra red band retained over diel cycle, Stauffer, 1980a) approximately 0.6 days are required for each meter of lake mean depth to attain the 4°C mark during mid-April in Wisconsin. For lakes Mendota ($\bar{z} = 12.4$ m) and Big Green ($\bar{z} = 31.0$) the expected lengths of the vernal convective circulation periods are approximately 7 and 19 days for mid-April insolation of ~500 cal $cm^{-2}d^{-1}$.

3. Windwork-Forced Overturn

After the lake attains 4°C, further additions of heat create upper layer buoyancy stabilization. Redistribution of this heat load downward requires expenditure of gravipotential work in the water column (Birge, 1916). This work is performed by the exogenous wind power time series above the lake. One laboratory-based model of this heat redistribution assumes that a small (~1%) but nearly constant fraction of the input kinetic energy of the wind is used to perform gravipotential work in the water column (Sundaram, 1973; Kato and Phillips, 1969; Kraus and Turner, 1967). Actually a fully generalizable lake transfer function model relating wind power to gravipotential work has never been adequately formulated and tested. Provisional estimates on Lake Mendota suggest that the work efficiency of the wind decreases by about 1 order of magnitude (from 3 to 0.2%) between late spring and early fall, accompanying the movement of the thermocline downward from ~3 to 15 m (thus further away from the wind energy source, Stauffer, unpublished data). At any given time, however, we do expect at least double the work for a doubling in input power. Such "mechanistic" model of thermal stratification interprets stratification as the dynamic interaction of two time series, namely the net heat (hence buoyancy) flux across the air-water interface (cal cm^{-2} s^{-1}) and the windpower time series (ergs cm^{-2} s^{-1}) (Sundaram, 1973; 1974; Tucker and Green, 1977).

4. The Dynamic Spring Period

If the date of ice-out is late (for example in May) the lake will not have attained the 4°C mark until a date when the radiation time series is already sinusoidally approaching its summer solstice maximum, and the wind power time series has already undergone its precipitous mid-spring attenuation in intensity (Stauffer, 1980b). Furthermore, the prevalence of extended spring season sequences of very low power (Stauffer, 1980b), accompanying atmospheric inversions over the lake surface, can result in the onset of permanent (even if only partial) thermal stratification soon after termination of the free convective circulation period. This tendency toward a short forced (wind driven) vernal circulation is marked for lakes at higher latitudes, lakes with small wind sheltered exposures, and especially lakes with large shoal areas and isolated deep holes of small areal extent. The extensive shoals trap the solar insolation in a narrow depth band, and accelerate the rate of surface layer heating. Fish Lake (see Table 1) typically stratifies in April for these last two reasons.

The specific lake heating process differs markedly from year to year because of pronounced variability in the late spring windpower time series. Figures 3-13 show the differential effects of wind during 1967, 1971-1973 on the onset of stratification in Lake Mendota. A long period of abnormally low windpower and warm sunny weather in mid-May 1972 resulted in full stratification prior to May 25 (Julian Day 145) for both Lakes Mendota and Delavan. A cool windy early June then deepened the thermoclines and cooled the epilimnions of these two lakes. The very windy May in the following year preserved nearly isothermal conditions in Lake Mendota until Julian Day 148. In both 1971 and 1973 marked thermal stratification only developed with the onset of sunny warm, relatively calm June weather. Conversely, June 1974 was cold and windy and Lake Mendota did not develop a typical summer thermal structure until early July. Strong stratification occurred early (May) in both 1975 and 1977. Notice that strong stratification set in on Lakes Mendota, Delavan and Green simultaneously following May 12, 1972. However, Fish Lake was already strongly stratified by that early date.

(text continued on page 21)

Table 1. Morphological characteristics of four Wisconsin study lakes and their drainage basins.*

Lake	County	Area (km²)	Max Fetch (km)	z_{max}(m)	V_L†	V_E†	A_{db} (km²)	$\frac{A_{db}-A_o}{A_o}$	$\frac{A_{db}-A_o}{V_L}$‡	$\frac{A_{db}-A_o}{V_E}$‡
Delavan	Walworth	7.19	5.0 SW-NE	17	54	42	103	13.4	1.77	2.30
Fish	Dane	0.88	1.5 E-W	18	5.3	2.6	*	**	**	**
Green	Green Lake	32.6	10.3 WSW-ENE	72	1010	233	274	7.4	0.24	1.04
Mendota	Dane	39.1	9.0 SW-NE	24	486	261	620	14.9	1.19	2.20

* After Stauffer (1974).

† Units = 10^6 m³; V_L = lake volume, V_E = epilimnion volume (above the 8.5 m plane except for Fish Lake (4.5 m plane)).

‡ Units = m^{-1}.

[Note: This is also the percent of the respective volume replaced by a land drainage basin water export of 1 cm.]

** Seepage lake; no surface drainage into lake.

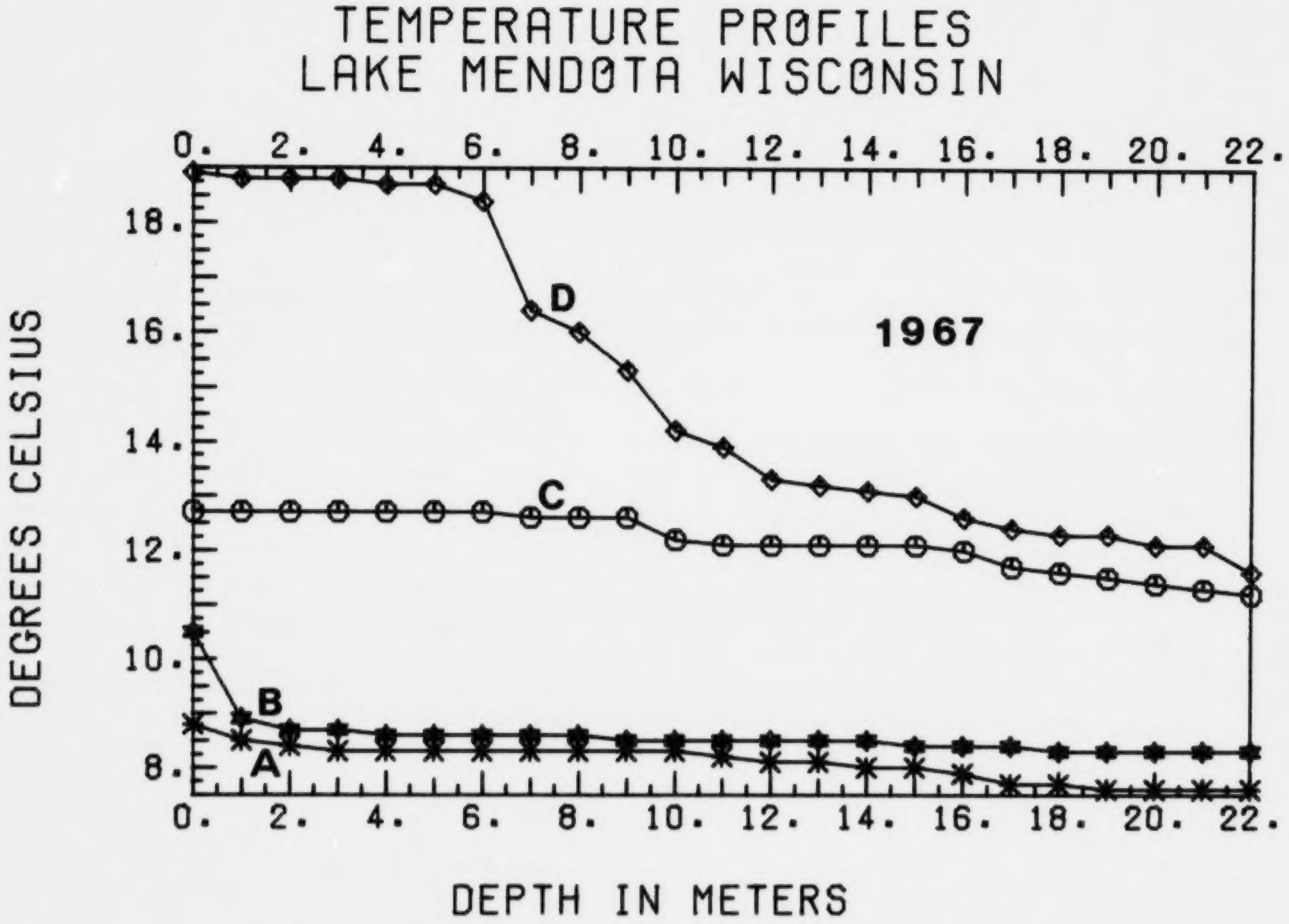

Figure 3. Lake Mendota thermal structure, Spring 1967: A) Julian Day 126, May 6; B) Julian Day 133, May 13; C) Julian Day 150, May 30; D) Julian Day 163, June 12.

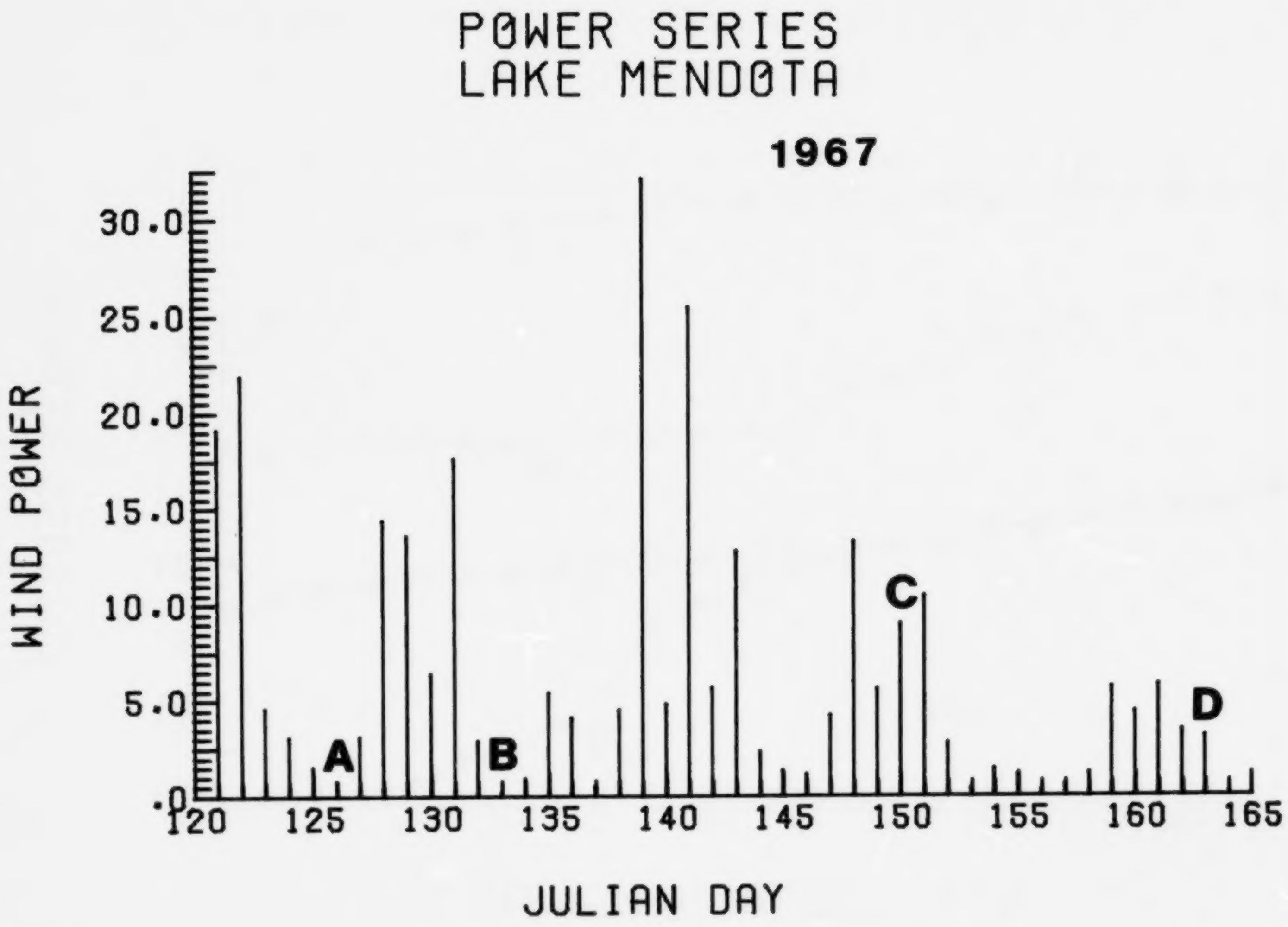

Figure 4. Madison daily windpower by Julian Day: 1967 (units: 10^5 erg cm^{-2} d^{-1}).

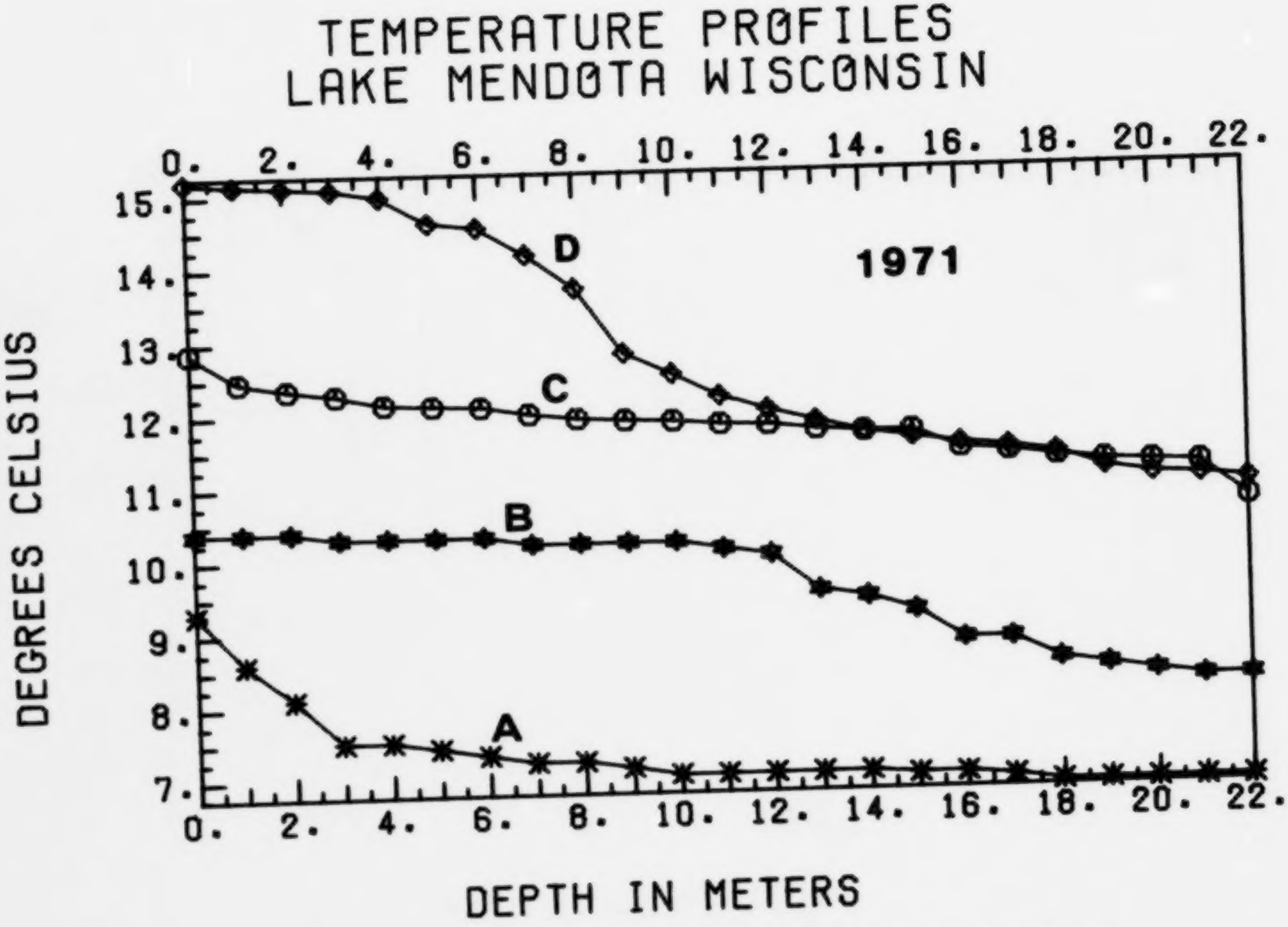

Figure 5. Lake Mendota thermal structure, Spring 1971: A) Julian Day 123, May 3; B) Julian day 133, May 13; C) Julian Day 148, May 28; D) Julian Day 154, June 3.

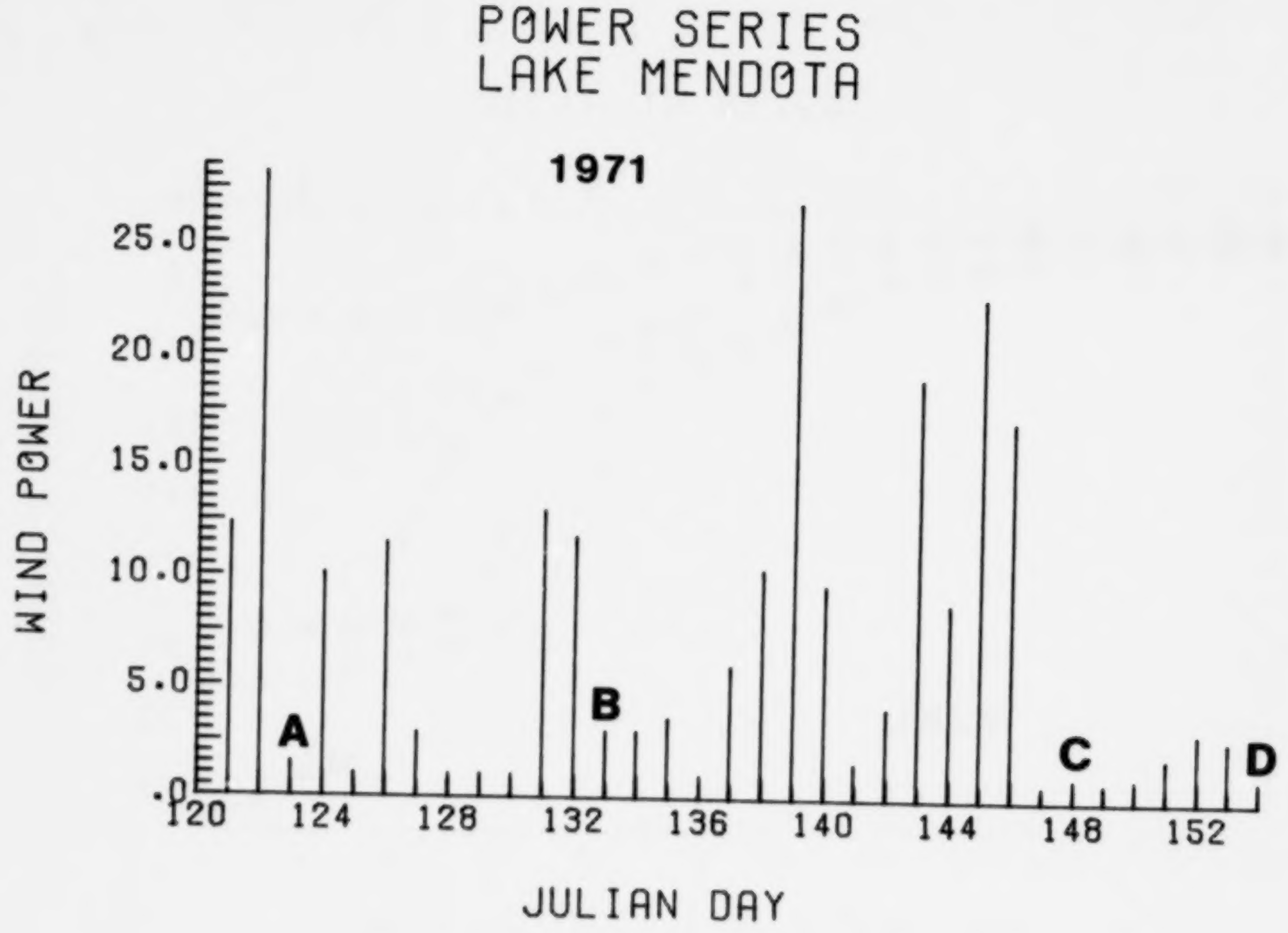

Figure 6. Madison daily windpower by Julian Day: 1971 (units: 10^5 erg cm^{-2} d^{-1}).

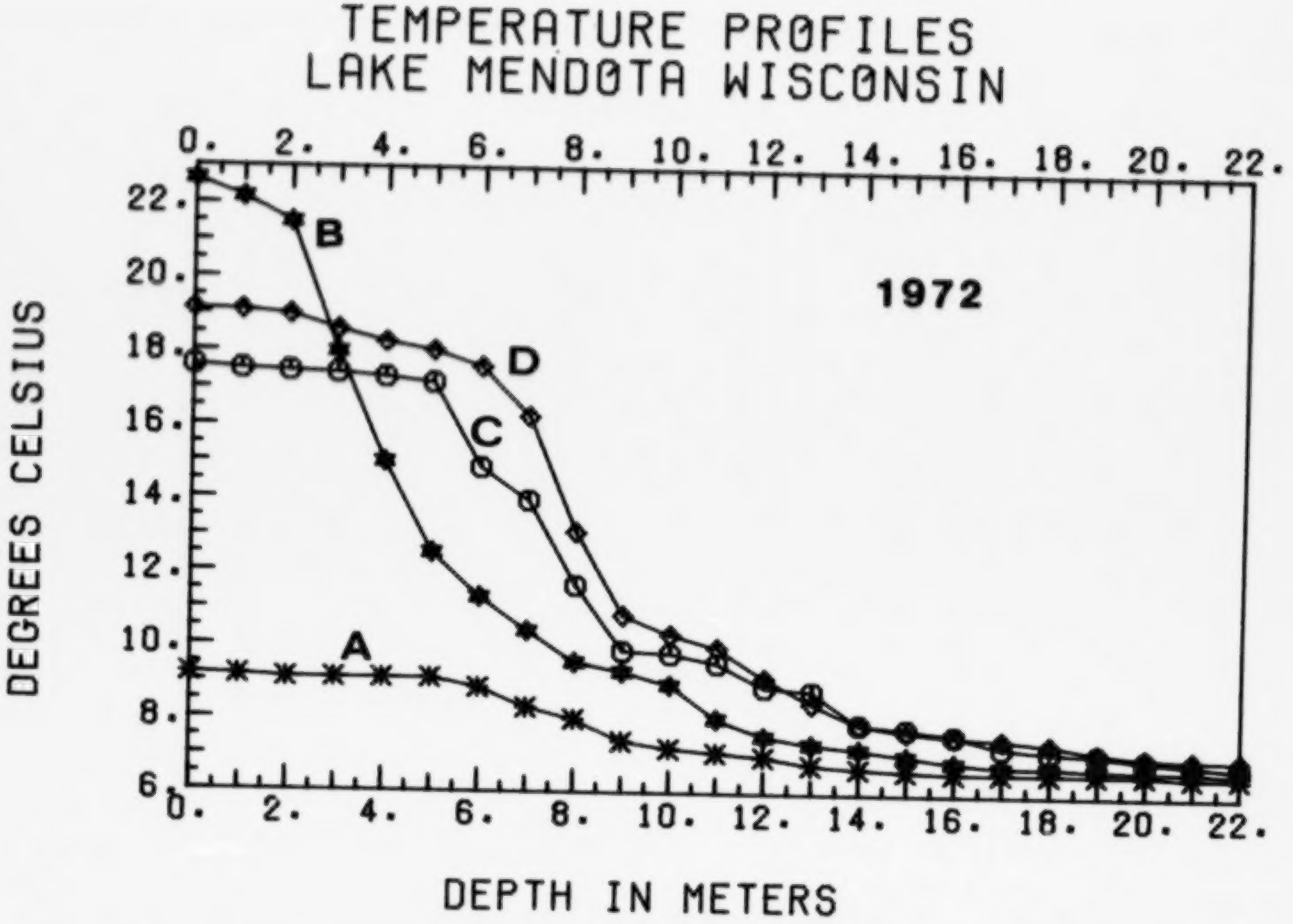

Figure 7. Lake Mendota thermal structure, Spring 1972: A) Julian Day 132, May 12; B) Julian Day 147, May 27; C) Julian Day 153, June 2; D) Julian Day 161, June 10. Note: on Julian Day 118 (April 28), Mendota was isothermal at 4°C.

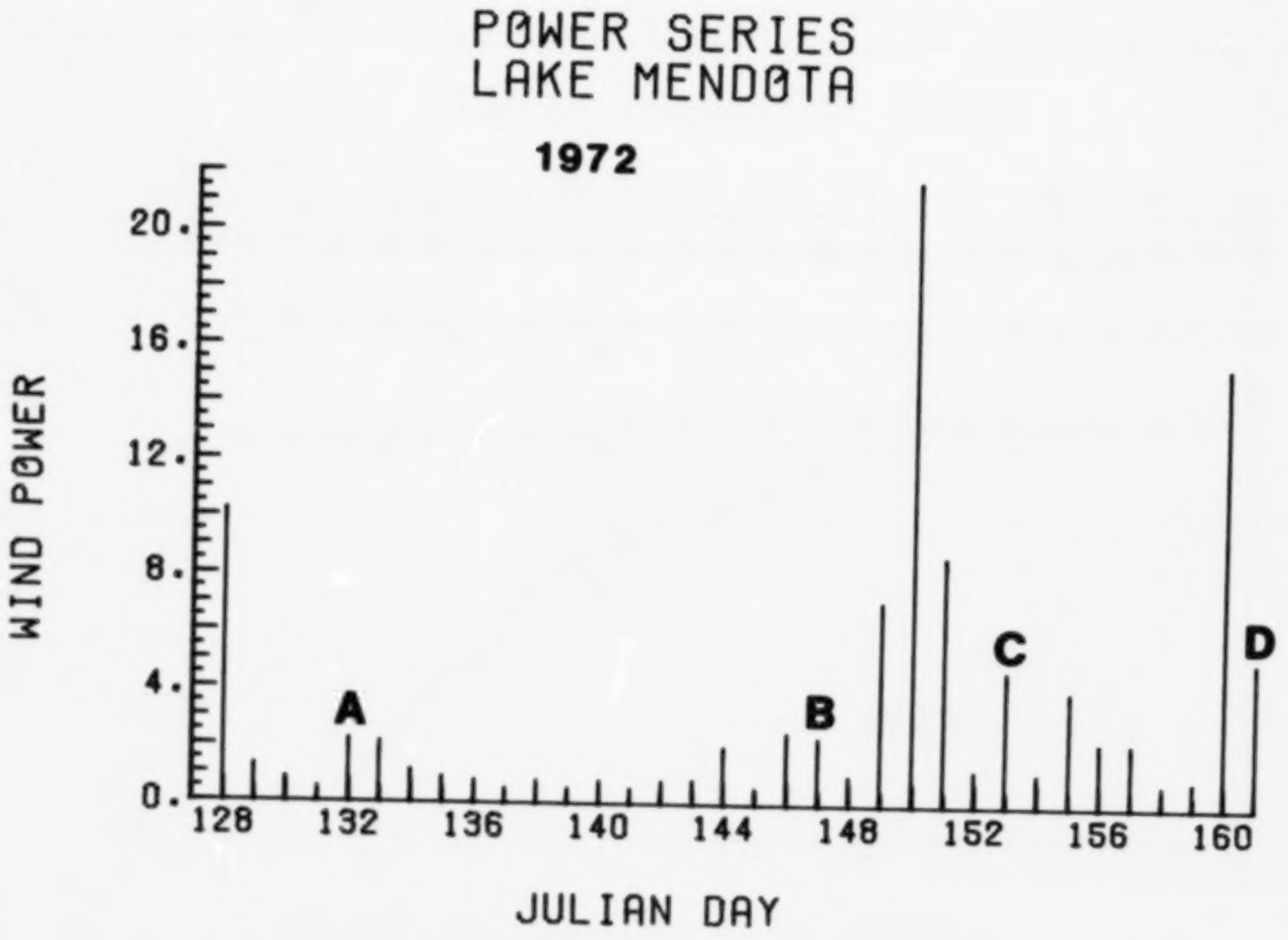

Figure 8. Madison daily windpower by Julian Day: 1972 (units: 10^5 erg cm^{-2} d^{-1}).

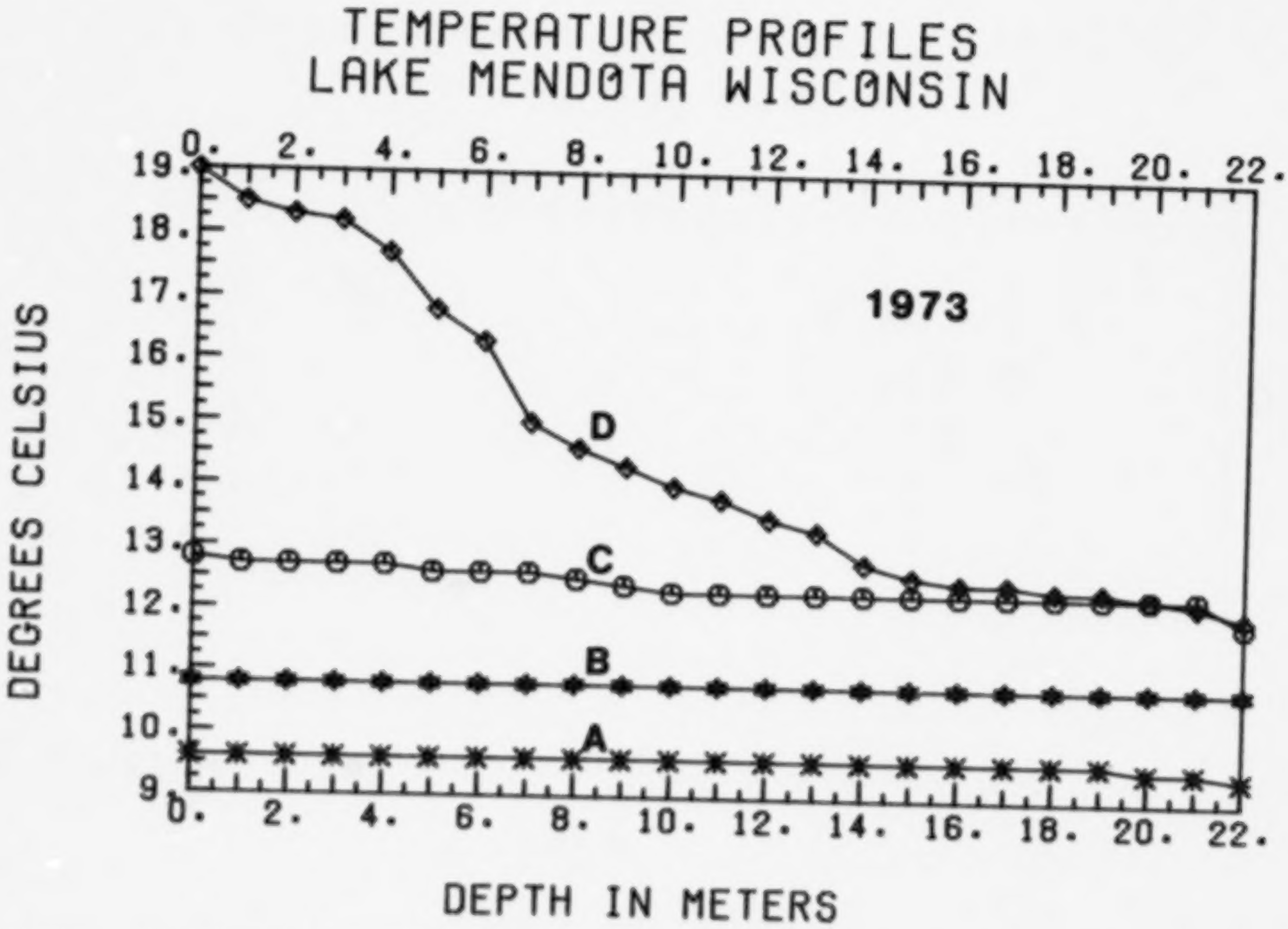

Figure 9. Lake Mendota thermal structure, Spring 1973: A) Julian Day 127, May 7; B) Julian Day 137, May 17; C) Julian Day 148, May 28; D) Julian Day 157, June 6.

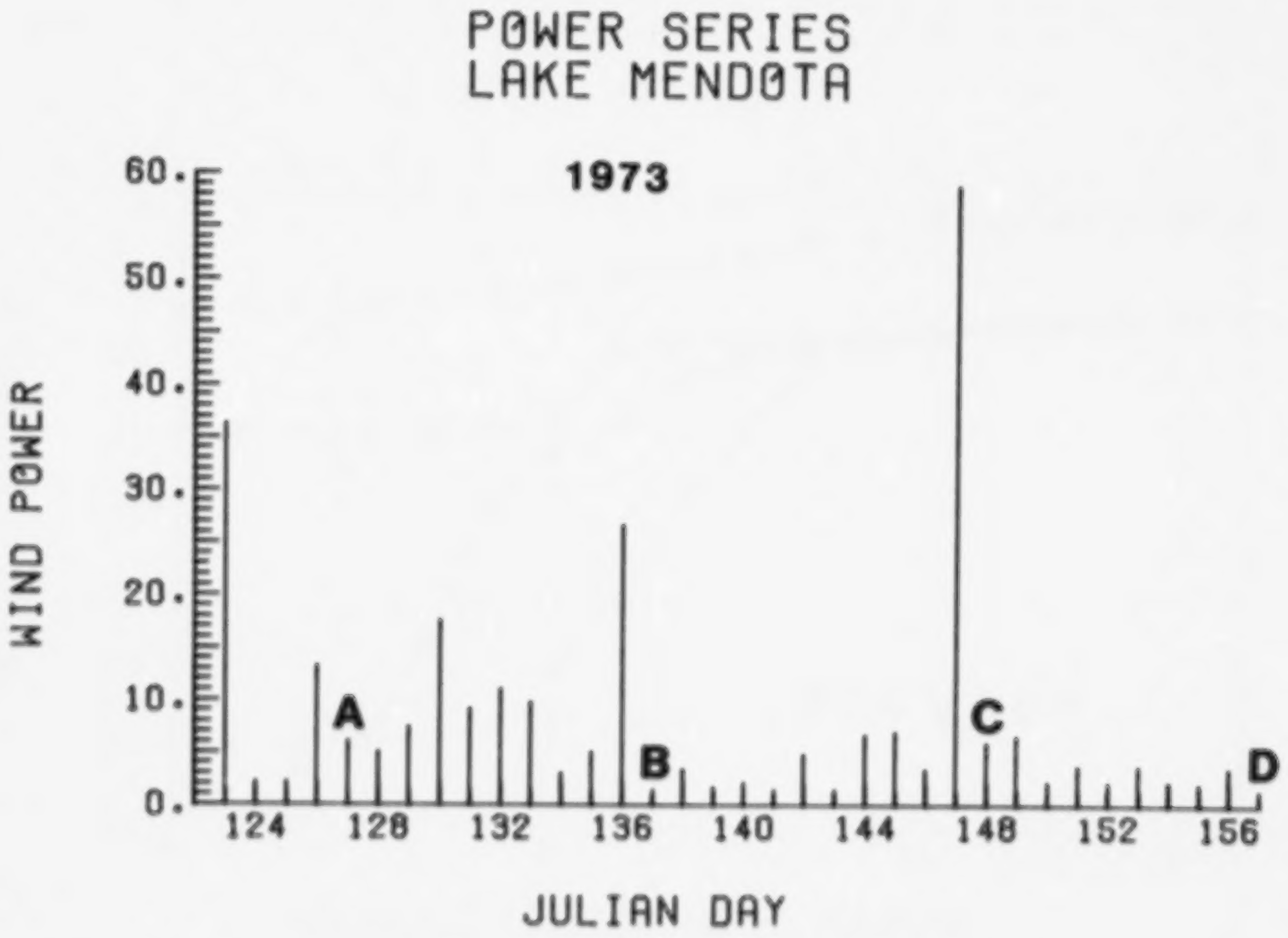

Figure 10. Madison daily windpower by Julian Day: 1973 (units: 10^5 erg cm^{-2} d^{-1}).

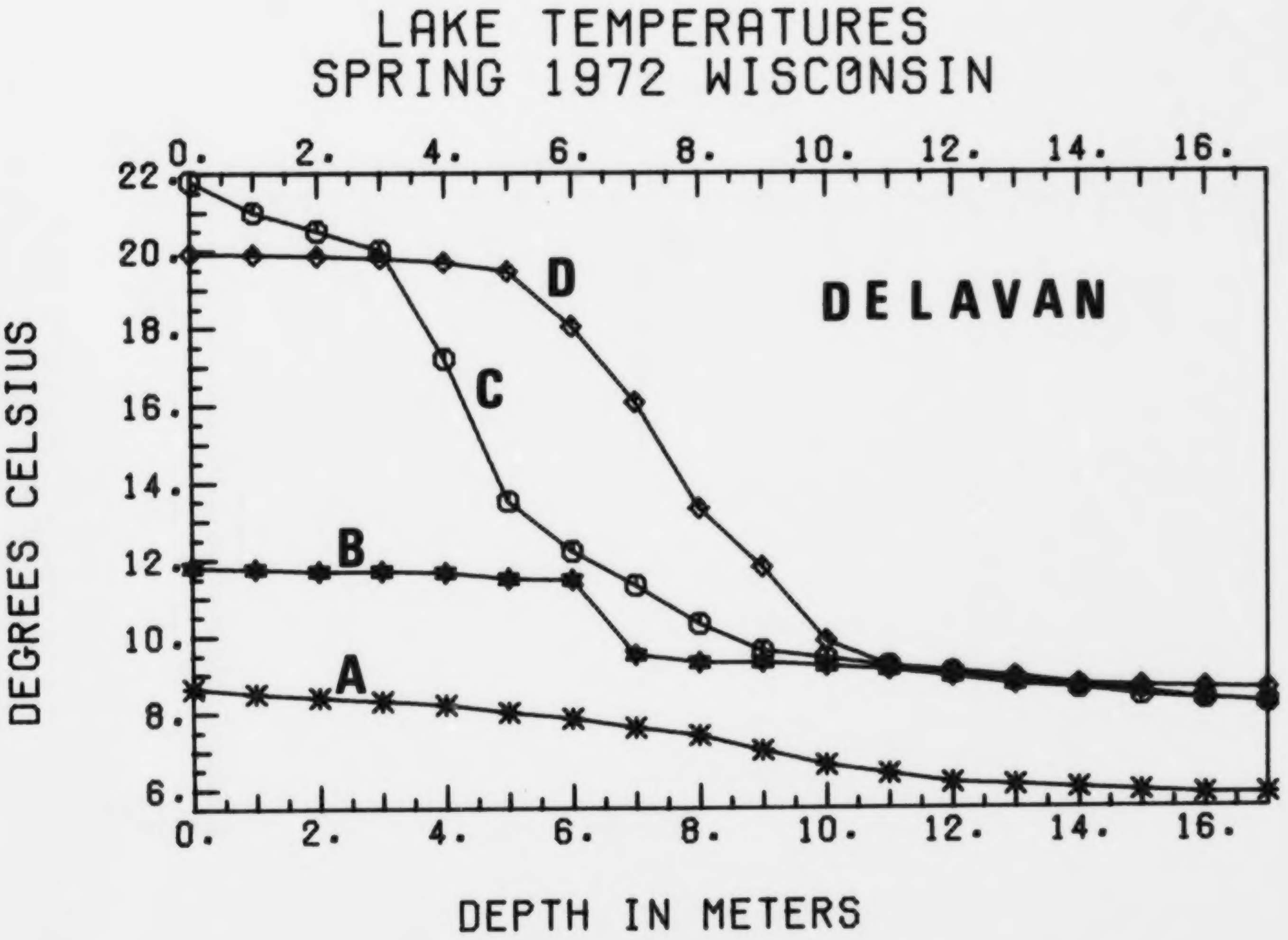

Figure 11. Lake Delavan thermal structure, Spring 1972: A) Julian Day 120, April 30; B) Julian Day 133, May 13; C) Julian Day 145, May 25; D) Julian Day 157, June 6.

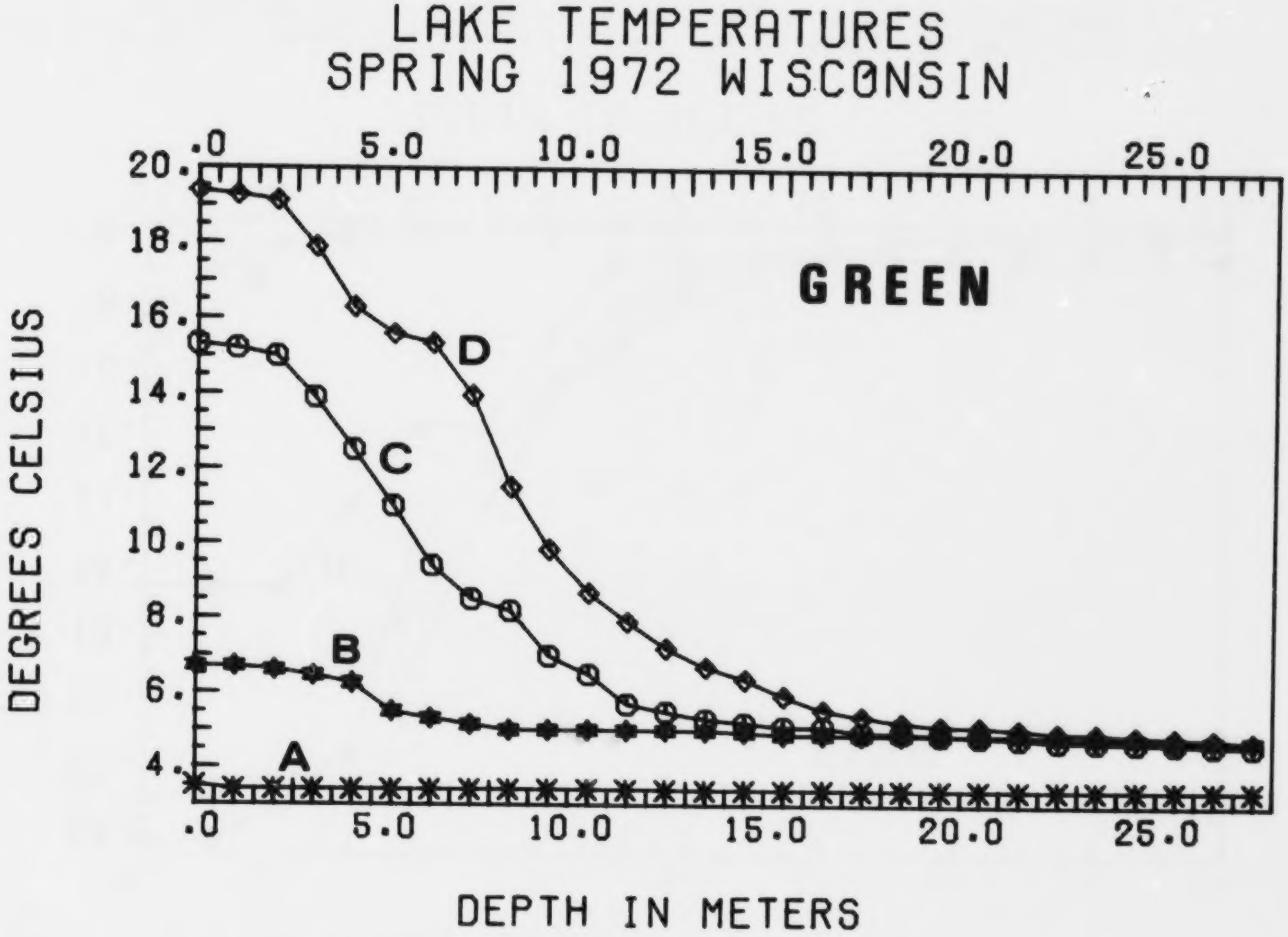

Figure 12. Green Lake thermal structure, Spring 1972: A) Julian Day 123, May 3; B) Julian Day 133, May 13; C) Julian Day 145, May 15; D) Julian Day 159, June 8.

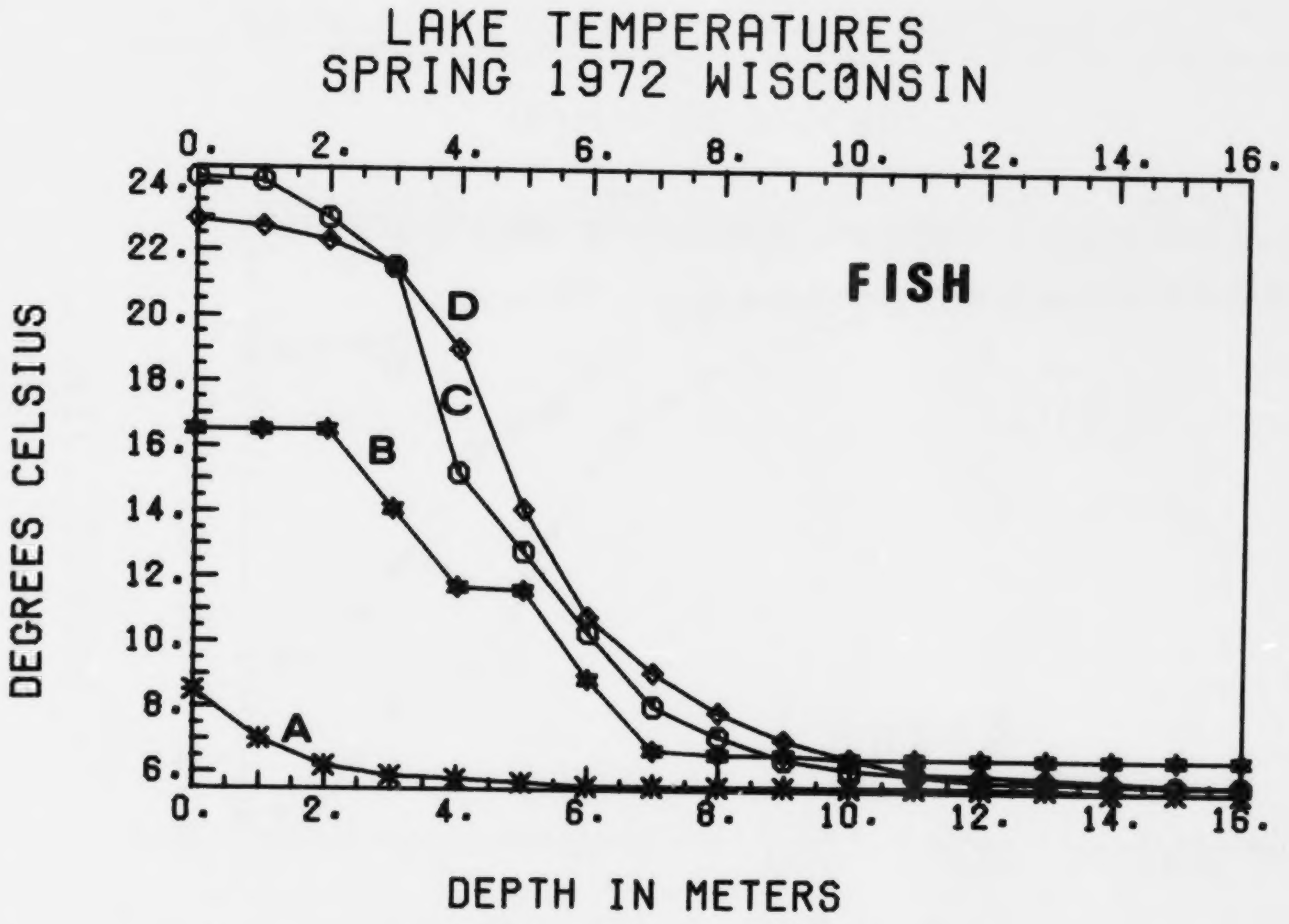

Figure 13. Fish Lake thermal structure, Spring 1972. A) Julian Day 119, April 29; B) Julian Day 132, May 12; C) Julian Day 146, May 26; D) Julian Day 158, June 7.

5. Classical Description of Stratification Thermocline

For lakes of sufficient depth, the spring dynamic heating period eventually makes a gradual transition to "summer stratification". The classical description (c.f. Hutchinson, 1957) or model of this stratification features a warm buoyant isothermal upper layer or epilimnion, which is circulated by the wind, and which "floats" on the colder nearly homogeneous hypolimnion bottom layer. The transitional layer separating the epilimnion and hypolimnion is called the metalimnion or "thermocline" where the temperature gradient exceeds 1°C/m. Because of the density stabilization within the thermocline, this layer is frequently considered to be a static diffusional barrier to vertical transport of heat and/or solutes between the hypolimnion and epilimnion, and vice versa.

The classical three layer description of summer thermal stratification is a useful model until misused in limnological research. Misuse involves the model's deficiencies. First the model has little to say about the complex sequence of events affecting the lake between ice-out and early summer. Second, it is a naively static interpretation of thermal stratification during the summer and early fall period.

6. The Summer Thermocline: Windpower and Air Temperature Stationarity: Heat Budget Equilibrium

The 2½ month period following mid June in Wisconsin is said to feature weather "stationarity" because of the absence of significant time trends in the important meteorological variables governing lake stratification and heat budgets (wind energy, insolation, relative humidity, air temperature). More generally, July-August is a stationary windpower minimum throughout the United States east of the Rocky Mountains. The weather stationarity period arrives earlier and persists later as we proceed along a transect from Wisconsin to the Gulf of Mexico (Stauffer and Dominguez, 1980).

After late June in Madison, Wisconsin the epilimnion has normally attained its "equilibrium" temperature of 23±1°C for the summer stationarity period. The epilimnion is in approximate thermal equilibrium with the atmosphere when daily heat losses via black body radiation and evaporation at the surface balance incoming radiation corrected for the albedo (6%). For lakes situated in humid temperate climates (3 PM relative humidity ~40%; 3 AM relative humidity ~80%) equilibrium is attained when the lake surface temperature is 1-2°C warmer than the average daily air temperature (Stauffer, 1980a). [Note: Because latent heat transfer increases linearly with both wind speed and the vapor pressure gradient (Deacon and Webb, 1962), lakes situated in arid windy climates will have cooler surface temperatures at equilibrium with the prevailing air temperature.]

During summer interludes of below normal air temperatures, above normal windspeeds, and/or below normal insolation, the epilimnion tracks the atmospheric trend and thus cools below its normal summer equilibrium temperature. A subsequent warming trend can then initiate new heat accumulations in the upper epilimnion and lead to the formation of multiple thermoclines. [This process has been well described by Lewis (1973) for tropical lakes. I follow his terminology.] Such weather trends during mid summer are capable of shifting Lake Mendota's surface temperature over 7°C (approximately 20 to 27°C). During a Midwest warming trend it is not unusual to have a high-lying daytime "breeze thermocline" positioned at 3 to 6 m and featuring a temperature drop from ~25°C to 21°C. This overlies the main "storm thermocline" beginning at z=8 to 10 m and 20 to 21°C. The storm thermocline encompasses an 8 to 10°C temperature drop in a 4 to 6 m depth interval. During subsequent windy cooling trends the "breeze thermocline" is both eroded and pushed downward until it is merged with the storm thermocline. Under favorable circumstances multiple thermoclines persist in Lake Mendota for several weeks.

The development of multiple thermoclines leads to a complex vertical partition of the nutrient store in the lake, and complicates procedures for estimating the magnitude and ultimate fate of internal (sediment-derived) supply. The complications include the following: First, the higher lying thermocline may partially overlap the trophogenic zone, hence sediment-derived nutrients may be utilized before their accumulation is apparent. Second, a high lying thermocline may persist long enough to initiate sediment phosphorus release but be transitory enough to be missed in a crude monitoring program. Third, the breeze thermocline is subject to large amplitude lateral tilts in response to wind stress (see later section).

7. Time Series for the Convective Circulation Depth: $h_c(t)$

Because the joint lake water-lake sediment system loses heat by black body (long wave) radiation and evaporative cooling only at the water's surface, but gains heat by the absorption of solar radiation at depth, the energy budget equation dictates that $h_c(t)$ is >0. The depth of convective circulation thus depends sensitively on: (1) the instantaneous balance between insolation and combined surface heat losses; (2) the extinction coefficients for light in the water column (c.f. Kraus and Rooth, 1961). During still sunny conditions at mid-day the high insolation "overloads" the water column by vastly exceeding surface heat loss rate. The result is a shallow convective circulation depth (perhaps only a few mm if the lake surface is cold and the insolation intense). However, at night, when insolation drops to zero, the convective circulation depth deepens sufficiently to satisfy the net surface heat exports (to the atmosphere) while maintaining a nearly isothermal profile above $h_c(t)$. After the lake attains summertime thermal equilibrium with the atmosphere over a typical diel cycle (net daytime heating balanced by net nighttime losses) the nocturnal convective circulation depth will coincide with the lower boundary of the epilimnion, hence upper boundary of the thermocline. Clearly, the diel maximum in $h_c(t)$ is shortly after sunrise, i.e., after the maximum duration of antecedent nocturnal cooling. Thermal studies on Lake Mendota, Wisconsin (Stauffer, 1980a) show that typical net heat losses between a mid afternoon sampling time of 1500 hr LST and 0700 LST the following morning average 200-250 cal cm^{-2} lake surface during the summer stationarity period. Assuming a vertical sided lake, a nocturnal loss of 250 cal cm^{-2}, and an isothermal afternoon epilimnion 5.0 m in thickness, then nighttime cooling will extend the isothermal mixed zone to 5.48 m by sunrise of the following morning (Figure 14) if the temperature gradient in the thermocline is 1°C/m. This example shows that the true diel mixed layer thickness is deeper than normally supposed based on mid-day or afternoon lake surveys. Assuming the same initial stratification conditions, then under conditions of sharply accelerated surface heat loss (as for example during cold fronts with high winds) the diel shift in $h_c(t)$ can be twice as large. The vertical amplitude of $h_c(t)$ migration is increased in lakes with extensive shoal areas because of their reduced water column heat capacities relative to lake surface area (heat losses are proportional to A_0). An example is shown in Figure 14.

The presence of weather cycles of longer than diel period (Stauffer, 1980b) guarantees that the summer time series of $h_c(t)$ is actually much more variable than the diel example illustrated above. Consider, for example, possible effects of the ~7 day cold front cycle on estimation of mixed layer thickness. If, as is so often the case, the lake sampling program is rigidly scheduled on a weekly basis, we have the maximum potential for statistical confounding between effects of the potential weather cycle and the sampling schedule. Stauffer (1980b) showed that following the cold front with its high windpower, low insolation, and frequently reduced relative humidities (all conditions favoring downward migration of $h_c(t)$), a period of high insolation and very low power often ensues. During this several day power interlude, the increased insolation and reduced evaporative cooling can result in reformation of a high-lying thermocline and upward migration of $h_c(t)$ from the upper boundary of the deep storm thermocline. In a typical midwest lake like Mendota or Shagawa Lake, Minnesota, $h_c(t)$ can vary from a few cm to ~10 m during the course of a few weeks in mid-summer. The importance of the $h_c(t)$ time series cannot be overemphasized in estimating the magnitude and interpreting the fate of internal nutrient sources in stratified lakes!

D. Biological Partitioning of the Water Column

The upper biological compartment in the lake is the "euphotic" zone or trophogenic layer. This extends from the lake surface to the "photo compensation depth" (here called h_e). At the compensation depth photosynthesis is just balanced by respiration over a typical diel cycle. This lower boundary is frequently assumed to the depth of penetration of 1% of the incident radiation (lake surface) in the visible region of the spectrum.*

The depth of the euphotic zone depends both on the lake surface albedo and the extinction coefficients for light in the water column. The effective albedo (fraction of incident radiation reflected) of snow-covered lake ice can be very high ($\gtrsim .95$), thus effectively suppressing primary production and nutrient uptake under the ice. The albedo drops as the snow cover decreases, and the ice takes on its bruised-blue color accompanying columnar recrystallization in the weeks just prior to ice-out. After ice-out, albedo averages

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* Note: In small sheltered lakes photosynthetic bacteria are frequently active at depths corresponding to ~0.1% of the visible incident light flux. The effective utilization of such low light levels may depend on the low water temperatures in such environments (reduces respiration rate) (T. D. Brock, personal communication, University of Wisconsin, Department of Bacteriology, April 1980).

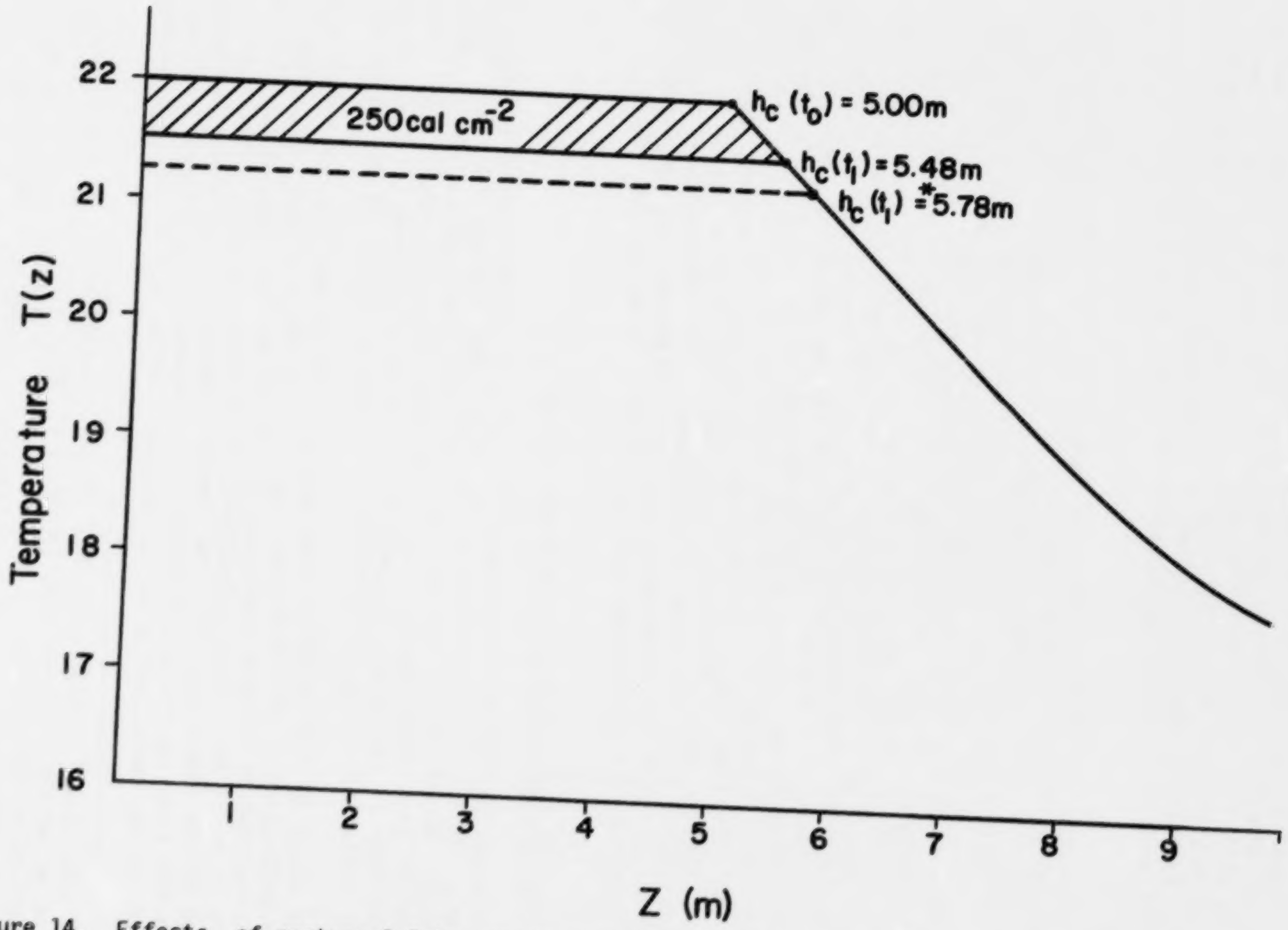

Figure 14. Effects of nocturnal lake surface cooling on the convective circulation depth. The dashed line corresponding to $h_c(t_1)^*$ shows overnight deepening if one-half lake area is 1 meter deep.

0.06 and is notably insensitive to meteorological conditions (Stauffer, 1980a). The ice albedo and available insolation are important environmental factors limiting algal development and nutrient uptake prior to ice-out. This is true because thermal stratification (below 4°C) under the ice preserves algal cells close to the ice window for light.

After ice-out the extinction coefficients for light in the water column control the depth of the euphotic zone. James and Birge (1938) (c.f. Hutchinson, 1957 for summary) showed that the natural yellow-brown-stained humic material in some forest or bog lakes is highly efficient in removing the bluelight which is otherwise most penetrative in pure lake water. A lakewater with 50 chloroplatinate units of natural color will have a photo compensation depth (defined as 1% of the visible) of $\lesssim 1$ m, even in the absence of any algal or inorganic turbidity.

Under favorable circumstances the euphotic depth (plane of 1% remaining visible) can be estimated as 2.5 times the secchi disk transparency (Tyler, 1968). This extrapolation is relatively imprecise, and is, in fact, inaccurate if the spectral properties of the water below the secchi transparency depth are different than in the upper portion of the water column. The extrapolation is good if $h_e < h_c$, i.e., if the estimated euphotic depth is less than the mixed layer depth. However, in small clear water (typically seepage) lakes with shallow thermoclines and metalimnetic chlorophyll maxima (Stauffer, 1980c; Fee, 1976), extrapolations based on the secchi disk transparency overestimate the euphotic depth. In this situation the all-important light extinction coefficients should be measured directly, using an underwater photometer (Bachman and Goldman, 1965; Jassby and Powell, 1975).

Above the compensation depth the time series for nutrients are influenced both by algal uptake and utilization and algal remineralization by zooplankton and bacteria. Below the true compensation depth is the "tropholytic layer" where the time series for nutrients depend on remineralization of sedimenting organic matter, degradative losses (for example, denitrification), chemical precipitation, sediment-water relations, and differential inter-layer vertical transport within the water column.

In large deep lakes vernal plankton blooming depends on the formation of a shallow "mixed layer" so that phytoplankton cells are preserved in the euphotic zone (Sverdrup, 1953; Riley, 1965; Lorenzen and Mitchel, 1973). This retardation of the vernal bloom can be exploited in sampling strategies designed to estimate the average nutrient potential of the lake after export of nutrients from the drainage basin has subsided, but prior to significant utilization of the lake nutrient store by algae. For Big Green Lake, Wisconsin the late ice-out and long free convective circulation period extend past the probable end of the important drainage basin phosphorus export period! Following ice-out, windpower reinforces convective circulation in homogenizing the lake. This dramatically improves sampling efficiency while preserving the utility of the solute mass estimates!

E. Sediment-Water Relations

1. Overview

The sediment sub-system interacts with the overlying lake water by exchanging heat and solutes on a seasonal basis, and by acting as a partly reflecting-partly absorbing boundary for: (1) penetrative solar radiation; (2) kinetic energy contained both in the wind driven circulation and gravity wave field. The magnitudes of these exchanges depend on season and on the depth of overlying water. The above factors act over time to control bulk sediment chemical properties, sediment surface albedo, sediment temperature, sediment redox state, and mixing intensity in the sediment surface-benthic boundary layer.

2. Sediment Bulk Chemical Composition

a) Physical Resuspension-Deposition Patterns. Well consolidated "grainy" sediments act as an intact shearing barrier which enhances turbulence in the overlying water. Conversely, dissipation of energy contained in the surface gravity waves acts to rework shallow water sediments until only heavy, grainy particles remain. The darker-colored fine-grained particles are resuspended by the turbulence in the shoals, transported laterally to the pelagic lake region, and eventually irreversibly settled out. The depth of wave influence depends on the amplitude of the waves (Tucker and Green, 1977), hence on wind speed, wind duration, and upwind fetch length (Barber and Tucker, 1962) accompanying storms in the recent historical period. Strong wind influences imply sandy or pebbly shallow water sediments that are chemically and biologically relatively inert. They are not important sources for phosphorus.

As the depth of overlying water increases, the physical and chemical character of the sediments changes because of this "sorting" effect of turbulence. Total iron, P and Mn are usually strongly enriched in the deeper water surficial sediments (expressed as μg/gm dry wt basis), as compared to the shallow water sediments (c.f. Delfino *et al*., 1969; Williams *et al*., 1971c) because fine grained particles settling into the deep water have large surface to volume ratios. The surface coatings on clay minerals are sorption active hydrous Mn(IV) and Fe(III) oxides (Carroll, 1958; Jenne, 1968).

b) Phosphorus and Iron Fractions in Calcareous vs. Non-calcareous Lake Sediments. Following the initiative of soil science, limnologists have sought to chemically *classify* the heterogeneous phosphorus and iron contents of lake sediments. The classification is empirically based on chemical extraction procedures which separate the total reservioir according to mineral type and crystallinity. In particular, the extraction schemes focus on defining a "potentially mobilizable" sediment P (or Fe) fraction. The "potentially mobilizable" fraction is that portion which can be solubilized and exchanged with the overlying water column, or taken up by rooted aquatic plants under certain (specified later) redox, pH, and temperature conditions which are potentially realized in the lacrustrine environment.

The influence of overlying water depth on "potentially mobilizable" Fe and P is much more pronounced (Williams *et al.*, 1971abc; Bannerman *et al.*, 1974; Larsen *et al.*, 1980) than on elemental totals. This is particularly true of non-calcareous drainage basins, where detrital heavy-grained hematite and magnetite may accumulate in shallow water sediments. These "well ordered" iron particles are not surface active with respect to phosphorus and play no significant direct role in the phosphorus economy of the lake. For typical bicarbonate-buffered non-calcareous drainage lakes in Vilas-Onedia Counties in northern Wisconsin, Williams *et al.* (1971c) found that the "potentially mobilizable" (CDB extractable) Fe/P atomic ratio partitioned into two groups. The Group A ratios ranged from 3.3 to 9.7 and averaged 6.5; these were associated with the deeper water sediments in all of the study lakes. The Group B ratios ranged from 21 to 85 and were associated with shallower water sediments (3-10 m) *below* the depth of direct wave influence. The high ratios are extremely unfavorable for desorption of P. The much lower ratios found in Group A are also representative of calcareous drainage lakes from southern Wisconsin. However, in the calcareous lakes, the CDB extractable Fe/P ratio did not change with depth of overlying water, although deeper water sediments contain considerably larger quantities of both extractable Fe and P (Table 2).

In calcareous lakes, a significant, although still minor percent (14-33%) of the total inorganic P is present in the form of apatite [$Ca_5(PO_4)_3X$, where X is OH^- or F^-, i.e., hydroxy or fluoro apatite] (Table 2). Because the lake waters and sediment interstitial waters are generally supersaturated with respect to apatite, this phase does not dissolve and is an unimportant source of P for sediment-water exchange. The apatite has been shown to be mainly of detrital origin (drainage basin erosion) both here (Syers *et al.*, 1973) and in Lake Erie (Williams *et al.*, 1976). The authigenic formation of apatite is kinetically hindered in many lake systems.

Apatite is quantitatively unimportant in non-calcareous lake sediments of Wisconsin, in part because the small detrital fluxes of the mineral slowly dissolve in the slightly acidic-lower-Ca sediment environment. Thomas and Dell (1978) have described this diagenic relationship for Lake Superior sediments. Williams *et al.* (1971a) noted that oxalate extractions of sediment P include the apatite fraction whereas CDB extractions do not. Because the apatite in calcareous sediments is inert, the oxalate extraction overestimates "potentially mobilizable" P. In non-calcareous sediments lacking apatite, the oxalate and CDB extraction schemes yield essentially the same sediment P fraction.

As was inferred in the classical sediment-water investigations of Einsele (1936; 1938) and Mortimer (1941; 1942), the extraction studies of Williams *et al.*, (1971abc) have shown that potentially mobilizable sediment P is associated with amorphous Fe in both the calcareous and non-calcareous lake classes. Aluminum is a negligible "natural" control on P, in part because it is tied up as primary and secondary alumino-silicate minerals. Amorphus $Al(OH)_3$ formed after alum treatments is very effective at adsorbing phosphate. Like the apatite fraction, the quantitatively important organic-P fraction in the upper historical sediments is relatively refractory over the seasonal time scales of interest here.

Table 2. Sediment phosphorus fractions in calcareous vs. non-calcareous lakes.

Lake	Depth		Sediment $CaCO_3$ % (of dry wt)	Sediment						
					Inorganic P				Extractable	
				mg kg^{-1} dry wt						
					Fractions					Atomic
	Z_{Sample}	(m)Z_{max}		Organic P	I	II	III	Sum	Fe†	Fe/P‡
A. Calcareous										
1. Wingra	3	6	53	292	229	86	45	360	1,800	4.4
2. Monona	13	19	33	320	646	219	79	944	5,800	5.0
3. Mendota	22	24	30	423	775	119	81	975	8,600	6.1
4. Delavan	15	17	53	359	429	152	46	627	2,000	2.6
5. Delavan	11	17	55	305	371	156	37	564	1,400	2.1
6. Geneva	21	43	39	279	263	116	58	437	3,700	7.8
B. Non-Calcareous										
1. Crystal	17	20	<0.5	---	718	17	22	757	5,600	4.3
2. Crystal	11	20	<0.5	320	374	5	30	409	3,400	5.0
3. Trout-S	33	34	<0.5	540	3,025	103	33	3,160	51,000	9.3
4. Trout-S	32	34	<0.5	410	5,565	86	27	5,680	73,000	7.3
5. Minocqua-E	14	18	<0.5	230	6,680	70	22	6,770	66,500	5.5
6. Minocqua-W	9	18	<0.5	520	1,935	154	32	2,120	27,000	7.7
7. Tomahawk	22	25	<0.5	780	3,330	105	33	3,470	---	---
8. Shagawa	>10	14	<0.5	---	3,800	240	---	---	45,000**	6.6

Notes: * Fraction I is sum of NaOH + CDB extractable fractions. These are identified with short range (amorphous) Fe in sediments. Fraction II is HCl-P fraction identified with apatite. Fraction III is residual inorganic-P released from hot NaOH or Na_2CO_3 fusion treatments. See Williams et al. (1981a) for calcareous lakes. See Williams et al. (1971bc) for non-calcareous lakes in Vilas-Oneida counties, Wisconsin.

** Shagawa data from Larsen et al. (1980). Assuming oxalate-Fe fraction is 90% of total for these deep water sediments (see Williams et al., 1971c).

† CDB or oxalate extractable iron (CDB for calcareous lakes; oxalate for Wisconsin non-calcareous). The two fractions are approximately equal.

‡ Atomic ratio of extracable (CDB or oxalate) Fe to Fraction I of inorganic P.

The data of Table 2, while valuable, is at best, narrowly representative of Wisconsin lakes; it is inadequate for describing the stoichiometric relations between Fe and P in lakes of diverse geologic and cultural settings. Only "drainage" lakes are represented in the calcareous class, and of these only Lake Geneva has escaped intensive agricultural and/or urban-based cultural eutrophication. Lake Geneva is the second deepest lake in the state and has a small land drainage area. It is significantly spring-fed. Present day summer hypolimnetic oxygen depletion rates (Stauffer, 1978, unpublished data) are indistinguishable from measurements made by Birge in 1907 (Birge and Juday, 1911). By contrast, closely-neighboring Lake Delavan is the most impacted by cultural eutrophication among the lakes listed in Table 2. In addition to extensive agricultural and suburban drainage (see Table 1) it has been severely impacted by direct sewer discharges from Elkhorn city (population 1970 = 40,000) for many years (Stauffer, 1974). The "Yahara Lakes" studied (Mendota, Monona, Wingra) currently receive varying amounts of agricultural and urban drainage (c.f. Ahern, 1976; Kluesner, 1972; Lathrop, 1978), and in the past municipal sewage (Mendota, Monona) (Sonzogni and Lee, 1974).

In light of these historical impacts it is interesting that Lake Geneva has the highest sediment extractable Fe/P ratio, while neighboring Lake Delavan has by far the lowest ratios among all the lakes studied by Williams et al. (1971c). If accurate, the 11 m Delavan ratio is only 40% greater than the stoichiometry of vivanite, $Fe_3(PO_4)_2 \cdot 8H_2O$, the lowest stoichiometry iron phosphate mineral stable in reducing sediment environments, and a known diagenic product in both calcareous and non-calcareous lake sediments (Tessenow, 1974; Emerson, 1976; Emerson and Widmer, 1978; Anthony, 1977). Furthermore, the Delavan ratios are less than one half of lower bound stochiometric ratios for PO_4-P adsorbed on amorphous preformed hydrous Fe(III) oxides at neutral pH (Einsele, 1936; 1938)! Under alkaline pH the adsorption of PO_4-P on these oxides is still less favorable (Einsele, 1936; 1938).

The second lowest extractable Fe/P sediment ratios apply to eutrophic Lake Wingra. Williams et al. (1970) found that Lake Wingra sediment has by far the lowest tendency to adsorb added PO_4-P among all the lakes they studied (Delavan was not studied), and desorbed the largest fraction of this adsorbed P during a subsequent desorption step.

The non-calcareous lakes studied from the Northern Highlands State Forest (Table 2) are representative of bicarbonate-buffered natural forest drainage and seepage lakes experiencing negligible or only minor (except Minocqua West) cultural influence. Trout Lake retains the hypolimnetic oxygen relations (Stauffer, unpublished data, 1978) reported earlier by Birge and Juday (1911). Minocqua West formerly received sewage from the towns of Woodruff and Minocqua. The Wisconsin lakes investigated have low natural color (chloroplatinate units) hence are unrepresentative of lakes subjected to drainage from acid sphagnum bogs and tamarack-spruce swamps. Both the total and soluble Fe/P ratios from lakes and streams in this latter class (Table 3) are an order of magnitude higher than the sediment extractable ratios for non-calcareous lakes reported in Table 2 (Stauffer and Armstrong, 1980a). Four meromictic lakes in crystalline drainage basins of southern Norway are noteworthy for their high sediment atomic Fe/P (totals) ratios (c.f. Table 4) (Kjensmo, 1967). Similar conditions have been reported from the Experimental

Lakes Area of Western Ontario (D. W. Schindler, personal communication, 1979). Crystal Lake is among the most oligotrophic lakes of the state and yet has the lowest extractable Fe/P ratio among the non-calcareous lakes. The lake has negligible drainage basin influence except direct atmospheric deposition on the lake surface, hence extremely low Fe, SiO_2, and Ca sediment deposition rates (Twenhofel and Broughton, 1939) and almost undetectable free water concentrations of Fe, SiO_2 and SRP (Stauffer, R.E., unpublished data, 1978).

Table 3. Concentrations of Fe, Mn, P in Representative Surface Waters of the Forested Northern Highlands Region, Wisconsin and Northern Minnesota.

Sample Sources (date)		Total			
		Fe mg m^{-3}	Mn mg m^{-3}	P mg m^{-3}	Fe/P (atomic)
1. Allequash Cr., WI*	UA	340	46	21.5	8.7
9/3/79	FA	(260)	(31)	(14.0)	10.2
2. Stevenson Cr., WI	UA	910	31	14.0	36.0
9/3/79	FA	(700)	(31)	13.0	30.0
3. Cranberry Cr., WI	UA	5,780	46	41.5	77.0
9/12/79	FA	(1,980)	(62)	35.5	31.0
4. Burntside R., MN*	UA	75	17	2.0	19.0
8/3/79	FA	<35	<8	3.0	---
5. Armstrong Cr., MN	UA	1,100	405	15.0	41.0
8/3/79	FA	(835)	(370)	14.0	33.0
6. Helmet Lake, WI	UA	725	46	15.5	26.0
9/4/79	FA	(590)	(46)	13.5	24.0

* Low color, lack bog drainage.
UA = unfiltered acidified; FA = filtered acidified.

The extractable Fe/P ratio estimated (see Table 2 notes) for Shagawa Lake's 12 m and 14 m deep holes may be too high given the important hematite mineralization in the Vermillion Iron Range forming part of its drainage basin, and the large fraction of non-extractable Fe and P at lesser overlying water depths. Cultural eutrophication of the lake has markedly decreased the Fe/P ratio in the surficial sediments (Larsen *et al.*, 1979; 1980).

c) Summary of Factors Controlling Fe vs. P Sedimentation. Summarizing, the main geochemical determinants of sediment Fe-P relations are as follows. The extractable Fe/P sediment ratio reflects both the relative strengths of the external sources for non crystalline Fe vs. P, and the

Table 4. Total Iron, Manganese, and Phosphorus in Representative Calcareous vs. Non-calcareous Deep Water Lake Sediments*

	Lake	Sampling Depth (m)	z_{max}	Organic Carbon	Fe $mg\ G^{-1}$	Mn $mg\ G^{-1}$	P $mg\ G^{-1}$	Atomic Ratios Fe/Mn	Atomic Ratios Fe/P	Atomic Ratios Mn/P
	A. Calcareous									
1.	Mendota[BL]	23.2	24.5	84.0	19.0	1.5	1.95	12.5	5.4	0.44
2.	Mendota[BL]	18.6	24.5	77.0	22.0	1.05	1.60	20.7	7.7	0.37
3.	Monona[B]	~19.5	19.5	---	18.0	.8	1.75	22.1	5.7	0.26
4.	Monona[B]	16	19.5	74.[W]	18.5	.75	1.80	24.3	5.7	0.24
5.	Wingra[B]	3.4	6.0	71.0	8.5	.56	.63	15.0	7.5	0.50
	B. Non-Calcareous									
1.	Trout-South[B]	34	35.5	157[W]	66.0	4.0	7.6	16.2	4.8	0.30
2.	Trout-North[B]	28	28.5	---	68.0	3.8	10.0	17.6	3.8	0.22
3.	Minocqua-SW Bay[B]	13.7	14.0	160[†]	60.0	1.95	9.3	30.3	3.6	0.12
4.	Firefly Lake[B**]	12.6	14.0	250‡	14.2	0.25	2.85	55.9	2.8	0.05
5.	Devils[B]	13.1	14.0	75[W]	36.0	0.46	2.40	77.0	8.3	0.11
6.	Shagawa (EEDH)[WW]	12.0	12.5	123[L]	58.0	0.97	6.0	58.8	5.4	0.09
7.	Shagawa (BPOH)[WW]	13.0	14.0	123	49.0	1.27	4.5	38.0	6.1	0.16
8.	Store Tryvann[K]	15.5	16.0	220	75.0	3.8	3.8	19.4	10.9	0.56
9.	Bjordammen[K]	13.0	13.5	248	75.0	7.5	3.5	9.8	11.9	1.21
10.	Skennungen[K]	17.0	17.8	220	97.0	0.7	2.6	136.0	20.5	0.15
11.	Store Aaklungen[K]	32.0	32.5	240	121.0	1.05	2.5	113.0	26.3	0.24
	C. Average World[K]									
	Igneous Rock	NA	NA	NA	51.0	0.93	1.31	54.0	21.6	0.39

* Surficial sediments collected by dredge except Mendota (top 5 cm of cores at overturn).

** Firefly Lake formerly called Weber Lake.

† 15 meter sample from East Basin used for organic C (Williams _et al._, 1970).

‡ Value for edaphically, morphologically similar Crystal Lake (Williams _et al._, 1970).
Data source: B-Bortleson (1970), BL-Bortleson and Lee (1972), K-Kjensmo (1967), L-Larsen _et al._ (1980), W-Williams _et al._ (1970), WW-Waddington and Wright (1974) except for organic C.

relative tendencies of these two elements to be immobilized by sedimentation. High drainage basin pH's (calcium related), low concentrations of dissolved humic coloring material in drainage streams, low erosion rates, and selective enhancement of the soluble phosphate flux via agricultural fertilization or sewage additions all act to decrease the Fe/P ratio by enhancing the drainage basin flux of P relative to Fe. The Fe is contributed by erosion of clastics (calcareous agricultural soils) or acidic chemical weathering involving humic materials (Northern Highlands). In the lake environment, high pH favors selective precipitation of Fe because phosphate sorption (on Fe(III) oxides) is unfavorable under alkaline conditions. Detrital apatite is unimportant in the phosphorus economies of calcareous lakes. In non-calcareous sediments it may slowly dissolve and release a Fe-active P component.

Within the lake the sediment resources of "potentially mobilizable" Fe and P usually increase dramatically in proceeding from the shallow to the deepest water sediments. The effect of overlying water depth is particularly striking in the final few meters. In those non-calcareous lakes that have received study the potentially exchangeable Fe/P ratio also shifts dramatically downward as the deep hole sediments are approached. In the calcareous lakes that have received study the reservoir of exchangeable Fe and P increases with depth but at a lesser rate than the non-calcareous lake class. Importantly, the Fe/P ratio is little affected, if at all.

3. Sediment Release of Dissolved Inorganic Phosphate

a) Fickian Diffusion Model. In principle the diffusion flux of phosphorus and other sediment solutes across the sediment-water interface can be described by Fick's first law,

$$J_s^{(z)} = K_s^{(z)} \frac{\partial s}{\partial z} \qquad (1)$$

where J has units: mM solute S cm^{-2} s^{-1}, K is the effective diffusivity for S along the z axis (units: cm^2 s^{-1}) and $\partial s/\partial z$ is the solute concentration gradient applicable to the interface. [In practice difficulties arise from trying to estimate the effective diffusivity and concentration gradients at the interface.] The Fickian model shows that flux is proportional both to the mixing intensity and the solute concentration gradient. Modeling sediment P release over space and time, thus, depends on knowledge of environmental control over these two parameters.

The concentration gradient depends on the solute concentration in the overlying water and the concentration in the sediment interstitial water. The latter is usually more important in determining the gradient. The interstitial inorganic phosphorus (IIP) concentration depends on the stoichiometric balance between Fe and P, redox, temperature, and diffusivities, at the interface, in the overlying water, and in the bulk sediment. The factors are inter-related. First I present a chemical model for interstitial phosphorus and Fe concentrations.

b) Chemical Factors Controlling Sediment Intersititial Phosphate and Fe(II) Concentrations. The importance of sediment redox potential on Fe, P, Mn, and SiO_2 sediment mobility was shown in the classical studies of Einsele (1936; 1937; 1938) on the non-calcareous Schleinsee in southern Germany and Mortimer (1941; 1942) on non-calcareous lakes of the English Lake District. When Eh falls below $\sim +100$ mv associated with the disappearance of detectable dissolved oxygen, Fe(III) present as amorphous hydrous oxide (CDB-Fe or oxalate-Fe fractions) is reduced and Fe(II) comes into solution. The solubilization of Fe also solubilizes the associated inorganic phosphate. Under low redox, interstitial concentrations of Fe(II) and PO_4 increase jointly until a solubility product involving reduced Fe is exceeded. The stoichiometric balance between Fe(II) and PO_4 in the interstitial water depends on the Fe:P stoichiometry of the oxidized iron undergoing reduction and dissolution, pH, and the availability of H_2S for forming FeS as a Fe(II) sink.

Ferrous iron readily precipitates with H_2S to form amorphous FeS, and the more highly ordered mackinawite (FeS), at pH's near neutrality (Einsele, 1938; Berner, 1964; 1967; 1970; Nriagu, 1968; Davison and Heaney, 1978; Stauffer and Armstrong, 1980a). In the presence of S^o formed by partial H_2S oxidation, these kinetically unhindered sulfide precipitates undergo a slow diagenesis to pyrite (FeS_2) which is a final stable iron reservoir in reducing environments (Berner, 1970). At pH 7.3 (a value representative of late summer conditions in the benthic hypolimnetic boundary layers of stratified calcareous lakes (Stauffer and Armstrong, 1980a) chemical equilibrium with respect to amorphous FeS implies only 12 µg Fe(II) L^{-1} present associated with 3.2 mg S(-II), actual late summer deep water concentration (Delfino, 1968; Stauffer and Armstrong, 1980a). Furthermore, pH's in the benthic hypolimnion boundary layer of bicarbonate-buffered non-calcareous lakes undergoing sulfate reduction increase to a value close to 7.15 (Davison and Heaney, 1978; Stauffer and Armstrong, 1980a) because of alkalinity increases associated with sulfate reduction (Goldhaber and Kaplan, 1973; Berner, 1970; Scholkovitz, 1973). Thus, for bicarbonate-buffered benthic environments, pH>6.5 and usually $\geq$7.0; both FeS solubility product considerations, and broad environmental experience (Stauffer and Armstrong, 1980a) prove that such anoxic hypolimnion waters can be classified as either sulfide rich or Fe(II) rich, but never simultaneously rich in both Fe(II) and total dissolved sulfide.

After the onset of anoxia the concentrations of Fe(II) and/or PO_4 increase until finally the ion activity product of Fe(II) and PO_4 exceeds the solubility product of a kinetically unhindered reduced iron phosphate mineral. Further increase in interstitial water concentrations of these solutes then stops. Vivianite, $Fe_3(PO_4)_2 \div 8H_2O$, is the least soluble reduced iron phosphate mineral. Because its formation is frequently kinetically hindered, reduced surficial lake sediments normally attain a metastable equilibrium with some unidentified amorphous gel-like solid phase which is more soluble than vivianite. In accordance with the solubility product principle, interstitial water equilibrium with respect to reduced iron phosphates can be attained for infinitely varying Fe(II)/IIP ratios. If the concentration of Fe(II) is held low by significant H_2S at near neutral pH's, the IIP concentration will be high. Conversely, high Fe(II) concentrations imply lower IIP at constant pH. If the pH drops, the concentrations of both Fe(II) and IIP must rise to satisfy the iron-phosphate and FeS solubility products because of increasing protonation of the PO_4^{3-} and HS^- ions as H^+ increases. Lowering the pH's can preclude attainment of FeS equilibrium for the available H_2S supply (see below) and thus uncouple Fe from its sulfide control. Acidic conditions thus mobilize *both* Fe(II) and PO_4 *simultaneously* in the sediment environment (c.f. Patrick *et al.*, 1973). Lower pH accounts for the coexistence of high concentrations of both H_2S and Fe(II) in mildly acidic (pH 5 to 6) lakes with acid-bog drainage in the Northern Highlands region of Wisconsin (Stauffer and Armstrong, 1980a). Meromictic Lake Mary is an example.

For pH's $\gtrsim 7.0$, the Fe(II) vs. H_2S "chemical exclusion principle" dictates that the interstitial dissolved Fe/P crossing the sediment-water interface depends on the *rate* of production of H_2S accompanying sulfate reduction as compared to the *rate* of supply of Fe to the interface. If sedimentation of drainage basin export Fe(III) is unimportant during stratification (this was shown to be true for seepage and drainage lakes in the Midwest during the *typical* summer) then the Fe can only be supplied from *below* the sediment-water interface.

Einsele (1938) showed that the oxidation of 10 mg L^{-1} Fe(II) to Fe(III) at pH 6 to 7 *in the presence* of 5.5 mg L^{-1} PO_4-P resulted in the formation of a yellow-white ferriphosphate precipitate of strengite-like composition (Fe/P = 1:1). These experiments were performed both in lake and artificial water systems with realistic bicarbonate buffering and Fe(II) initial concentrations ranging up to ~10 mg L^{-1}. The experimental domain was high but still representative of some reduced hypolimnetic and sediment interstitial waters. Furthermore, if Fe(III) as chloride salt solution was added to an adequately buffered natural water containing PO_4 the result was stoichiometrically the same. However, if Fe(III) was added to buffered water, or if Fe(II) was allowed to oxidze *in the absence* of PO_4, and immediately following the formation of the brownish hydrous Fe(III) oxide, PO_4 was added, the atomic Fe/P stoichiometry of the precipitate was changed to ~6:1 at pH's near neutrality. The adsorption precipitate did *not* alter to the ferriphosphate composition with aging. These observations by Einsele, and his related observations on FeS formation, are probably the most important chemical observations ever made on lakes. Tessenow (1974) conducted similar experiments using lower Fe(II) and PO_4 initial concentrations (1-2 mg L^{-1}) and obtained a precipitate with Fe/P = 1.7 at neutral pH. The ratio shifted slightly (to 1.8) at pH = 8.0. The precipitate was interpreted as approaching $Fe_2(OH)_3PO_4$ composition.

Based on the work of Einsele (1938), and the more conservative findings of Tessenow (1974), iron can quantitatively immobilize PO_4 as ferriphosphate in the upper water oxidation zone only if atomic Fe/P > 1.8. In other words, the potentially *free* migrating PO_4 (in terms of Fe chemical control) is given approximately by:

$$PO_4\text{-}P_{(free)} = PO_{4\ (initial)} - 0.55\ Fe(II)_{(initial)} : \text{if the R.H.S.} \geq 0$$

$$\doteq 0 : \text{otherwise (actually a few } \mu g\ L^{-1}\text{)}$$

The above equation is inaccurate for very low initial concentrations because the PO_4 concentration never falls completely to zero (Stauffer and Armstrong, 1980a).

c) Seasonal Model of Sediment Interstitial Fe and P Concentrations. The foregoing principles can be used along with other environmental variables to model sediment interstitial chemical composition on a seasonal basis. This chemical model provides insights into experimental studies of sediment release of P and lake budget studies on the ultimate fate of released P in the overlying waters. First, it is important to recognize that the sediment-water interface is not a razor-sharp diffusion boundary but rather a micro-stratified chemical interaction zone, whose thickness and position changes with season.

Assume, initially, following Mortimer (1971), that the "surface oxidized layer" is 1 cm thick, i.e., Eh falls to 0 mv at this level and, hence oxygen diffuses in 1 cm before being completely consumed. These conditions apply to mesotrophic Lake Windermere during winter (T_{sed} = 4°C). If these same sediments are close enough to the lake surface to be warmed to 24°C accompanying subsequent summer stratification, then, still assuming molecular diffusion rates, the new oxidized microlayer will have been reduced to 1-2 mm thickness. This reduction occurs because the temperature change decreases saturation oxygen concentration in the overlying water but enhances the O_2 diffusion rate commensurately (Lerman, 1979, p. 96). Meanwhile the rate of sediment BOD increases by perhaps an order of magnitude. The seasonal temperature shift alone has moved the upper boundary of the sediment reduced zone much closer to the sediment-water interface.

Now assume that algal production in the trophogenic layer commences and loads the surface of the sediment with readily decomposable organic matter. [Burns and Ross (1972) described algal-organic mats up to 2.5 cm thick being laid down on the surface of Lake Erie's Central Basin sediments.] The new organic layer adds an organic mat interface above the pre-existing historical sediment-water interface, and vastly increases the BOD rate at the new interface. The increase in "system" BOD rate is large because oxidation is "zero order" with respect to O_2 until low concentrations are reached, and because the BOD of the historical sediments involves relatively refractory organics (that is why they are still around). Because the only oxygen source in the sediment-water "system" is the bulk water column, the 0 mv Eh boundary shifts upward to the upper levels of the organic layer. Below this level SO_4 reduction commences in the middle-lower parts of organic layer, as SO_4 is the preferred electron acceptor after the consumption of initial O_2 and minor amounts of NO_3. Sulfate reduction is thus imposing a sulfide layer between the Fe-rich historical sediments and the overlying water column. Phosphate is generated in this multi-layered system both by mineralization of the organic matter (Richards, 1965; Richards et al., 1965) and diffusion up from the bulk historical sediments. Because the deposited algal remains are rich in P (~1% dry wt, Redfield et al. (1963)) but contain negligible Fe, remineralization yields a very low Fe/P ratio. Furthermore, the sulfide layer intercepts Fe(II) diffusing along with IIP from the sediments and precipitates it selectively as FeS. Phosphorus produced by remineralization is physically remote from a potential Fe interaction zone and IIP diffusing upward is liberated from its earlier Fe association. The overall result is a release of P into the bulk water column unassociated with Fe, and its relatively rapid transport up through the water column. This release occurs even if the overlying water column is saturated with dissolved oxygen!

The above scenario can be modified to reflect varying temperature conditions, eddy diffusivity rates for O_2 in the bulk water column, different O_2/SO_4 initial ratios, and varying organic deposition rates. Because O_2 is completely consumed before SO_4 reduction commences, a high O_2/SO_4 initial ratio may limit the sulfide production rate below the interface. Also colder water temperatures following complete fall turn-over will displace the sulfide boundary deeper into the sediment for reasons specified earlier. In marine waters (very high SO_4) the organic deposition rate is the critical parameter limiting sulfide production in the upper sediments. In sulfate-poor lakes in crystalline drainage basins the low SO_4 concentration in the overlying water ($\sim$3-5 mg L^{-1}) is limiting unless the lake is unproductive.

If the 0 mv Eh potential is near the surface of the historical sediment but the sulfate reduction rate is low, Fe(II) will come into solution in larger quantities than can be precipitated by the available H_2S supply. [Lowering the pH serves to decrease the effectiveness of the available H_2S supply.] In such cases the Fe/P ratio diffusing across the sediment-water interface may closely approximate the interstitial Fe/P ratio in the absence of sulfide influence. The ratio may approximate the CDB-extractable Fe/P ratio of the sediments, or be skewed if vivianite or similar minerals are forming with fixed compositions. In non-calcareous sediments the vivianite reaction will lead to interstitial Fe/P ratios that are larger than CDB or oxalate extractable Fe/P. In lake sediments with abundant FeS, PO_4 can "dominate" Fe(II) in the surficial sediments and vivianite formation can decrease the interstitial Fe/P ratio. Sediment composition (the potentially mobilizable Fe and P fractions), temperature, pH and rate of sulfide production are clearly the important variables determining the sediment Fe/P release ratio.

The "sulfide intercept" model just described may surprise some limnologists who are used to thinking rigidly of the "surface oxidized microlayer" as a "diffusion barrier" to phosphate release. The diffusion barrier model described by Mortimer (1971) is just the high Fe-low sulfate reduction end member condition of a much more general and valid model of sediment diagenesis. Stuiver (1967) showed that significant sulfate reduction occurred in the Linsley Pond (Connecticut) hypolimnion before the hypolimnion became anoxic. Einsele (1941) showed that fertilization of the non-calcareous Schleinsee with PO_4 caused a marked increase in organic production and hence an earlier onset of hypolimnetic anoxia as compared to prior years. However, the hypolimnetic release of Fe(II) decreased by 67% because of the formation of FeS stimulated by SO_4 reduction. These observations led Hasler and Einsele (1948) to propose lake fertilization with sulfate to stimulate PO_4 return from the sediment without associated Fe(II). This potentially uncouples the P cycle from its Fe-oxidation immobilization during the overturn. Ohle (1954) reiterated the theme. Hutchinson (1969) noted that enhanced sulfate reduction in Linsley Pond in recent years had accompanied post 1930's increases in lake sulfate content, a downward shift in the hypolimnetic Fe(II) release rate, and a pronounced upward shift in the H_2S and PO_4-P accumulation in the summer hypolimnion. More recently Stauffer and Armstrong (1980a) have shown that the Fe/P ratio of all calcareous lakes, and productive non-calcareous lakes, shifts downward during the summer as compared to winter stratification, and that the sulfuretum principle accounts for the especially high trophic efficiencies of calcareous lakes, generally. It has long been held that sulfide immobilization of Fe accounts for the high PO_4 contents of anoxic coastal fjords, ocean trenches and marine sediment interstitial water. The sulfuretum principle is probably partly responsible for the productivity of marine estuaries.

Studies of the sulfate-sulfide budgets of Lake Mendota (Nriagu, 1968; Stauffer and Armstrong, 1980a) and additional hypolimnetic sulfide data reported by Delfino (1968) and Delfino and Lee (1971), show that production of H_2S at the sediment-water interface is sufficient to ensure a net hypolimnetic ($z>15$ m) accumulation of 10-15 g S(-II) m^{-2} in the two month period following mid-July each year. This accumulation does not include sulfide formed but then oxidized by oxygen diffusing through the thermocline, nor sulfide immobilized as FeS and FeS_2 during the stratification period. However, the Mendota hypolimnetic accumulation is three times greater than the known sedimentary accumulation rate of FeS on an annual basis during the post-cultural period (Nriagu, 1968). Furthermore, the hypolimnetic excess is stoichiometrically (FeS) equivalent to all of the oxalate Fe fraction (including pre-existing FeS) in the top 3-4 cm of the hypolimnetic sediments of the lake. The sulfide production situation in Lake Delavan is even more extreme; hyoplimnetic concentrations at summer's end exceed 6 mg L^{-1} (Stauffer and Armstrong, 1980a). Sediment Fe capacity considerations thus conclusively show that H_2S production overwhelms Fe by a huge margin in the calcareous drainage lakes of southern Wisconsin. Furthermore, studies of sediment interstitial waters both in Mendota and the eutrophic calcareous Greifensee (Switzerland) show that sulfide production exceeds the potential Fe(II) diffusion rate in the upper 2 cm of the sediment by two orders of magnitude (Stauffer and Armstrong, 1980a)! The calcareous drainage lakes are thus "Sulfuretums". The same applies to mesotrophic calcareous seepage lakes (Stauffer and Armstrong, 1980a).

Under winter ice conditions sulfate reduction is low because of the very much reduced BOD loads placed on the deep-water sediments. Near the end of the ice-cover period we thus expect and find higher Fe/P ratios in the benthic boundary layer of calcareous lakes than during summer stratification (Stauffer and Armstrong, 1980a). This seasonal shift also applies to highly productive non-calcareous lakes. The oligo-mesotrophic clear water non-calcareous lakes of Northern Wisconsin have very low summer sulfate reduction rates because of limited SO_4 concentrations in the overlying waters (4 vs. 30 mg L^{-1}) and/or the much lower primary production-organic sedimentation rates as compared to the calcareous lakes (Stauffer and Armstrong, 1980a).

In completely oxidized littoral zone sediments PO_4 adsorption-desorption can control interstitial water concentrations and release into overlying water. The high pH's and low overlying water concentrations (PO_4) encourage release during the summer. The low concentrations in the overlying water necessary to support a concentration gradient are maintained by algal uptake. Release is most efficient with calcareous phosphate-enriched naturally Fe-poor sediments like Lake Wingra (Bannerman, 1973).

d) *FeS and Sediment Extraction Schemes*. The extractable sediment Fe/P ratios reported in Table 2 are misleading because they depend on procedures which were originally developed for aerated soils, not sediments; the extraction classification ignores the very important *competitive* (vs. PO_4-P) complexing of Fe by H_2S in anoxic lake sediments. Williams *et al*. (1971c) noted that oxalate extracts amorphous FeS, hence so does CDB (because CDB-Fe nearly equalled oxalate-Fe in calcareous sediments rich in FeS). Because Nriagu (1968) found that most sedimentary reduced sulfur in the post-cultural deep water sediments of Lake Mendota is present as FeS (not pyrite), the oxalate of CDB-Fe fractions estimate mainly FeS for the sulfur-rich gytta sediments in the calcareous drainage lakes. This is important because FeS has no affinity for PO_4. Nriagu (1968) reported that fully 27% of the *total* Fe in Mendota's post-cultural deep water sediments is tied up as FeS on an *annual* basis. Subtracting the FeS fraction from the oxalate-Fe reported for these same sediments by Williams *et al*. (1971c) leaves only 8-22% of the total Fe reservoir as the *potentially phosphate-active* iron fraction. Assuming an intermediate percentage (15%) I calculate an atomic: (oxalate-Fe minus FeS)/ CDB-P = 2.2 for Mendota instead of the 6.1 misleadingly shown in Table 2.

e) *Measurements of Sediment Phosphorus Release*. Direct measurements of sediment phosphorus release have been made either *in situ* using "sediment release chambers" (Sonzogni *et al*., 1977; Larsen *et al*., 1980) or in the laboratory using incubated *sediment-lake* water columns (Holdren and Armstrong, 1980). The laboratory technique, *while* seemingly less direct, is actually much more useful, both because it is cheaper, and because the pertinent environmental variables can be carefully manipulated and controlled to determine factor dependency of phosphorus (and other solute) release. [Note: It is important that lake water be used from the lake studied to preclude "unnatural" sediment-water chemical interactions.] The laboratory technique thus allows scientific exploration of a wide diversity of sediment-water environments, both germane to the heterogeneous sediment environments of a given lake, and potentially duplicative of remote or potentially existing (after lake change or dam construction, for example) lake sediment environments. For these reasons, and because of the extraordinarily interesting results, the recent study of Holdren and Armstrong (1980) deserves extensive comment and interpretation.

Holdren and Armstrong (1980) showed decisively that epilimnetic (3 to 6 m overlying water depth) sediments of calcareous drainage lakes (Wingra and Mendota) differed markedly from the non-calcareous lake sediments (Minocqua, Little John, Northern Highlands region) in terms of oxic SRP release rates. Laboratory attempts to reproduce truly anoxic conditions using N_2 flushing were not successful, as residual O_2 concentrations ≤ 0.8 mg L^{-1} always resulted in the overlying water. Previously, Mortimer (1941; 1942) experienced some difficulty in maintaining a truly anoxic environment in the laboratory.

For the non-calcareous lake sediments, lowered redox (overlying water) was a necessary condition for observing significant sediment P release. At 16-18°C oxic release rates were <0.6 mg SRP m^{-2} d^{-1}, and usually significantly lower. Furthermore, as initial SRP concentrations in the overlying waters were low, final concentrations were $\leq$ 40 mg P m^{-3}. Slightly higher release rates (up to 3.8 mg SRP m^{-2} d^{-1} at 16-18°C) were obtained under N_2 atmosphere (but retaining 0.8 to 3.9 mg O_2 L^{-1}). Release rates were negligible for water temperatures of 3-4°C, even if initial overlying water concentrations were $\lesssim$ 1 mg m^{-3}.

For the calcareous lakes the results were entirely different. Sediment P release increased dramatically with increasing core temperature and especially with level of benthic invertebrate activity. Invertebrate active Mendota cores collected throughout midsummer of two different years, and incubated at environmentally representative temperatures of 21-23°C, released vast quantities of SRP (20 to 83 mg P m^{-2} d^{-1}), irrespective of stirring rate of overlying water O_2 concentration. However, in the presence of the biocide, formalin, the oxic release rate (23°) dropped from 25 to 0.7 mg P m^{-2} d^{-1} in a specific core-core comparison. Final SRP concentrations in the oxic overlying water reached 688 mg m^{-3}! The IIP concentrations in the summer collected cores were generally high (>1000 mg IIP m^{-3}). [Note: These cores came from the epilimnion.]

By contrast, Mendota cores collected in midwinter and incubated at 2-4°C slowly liberated SRP (0.56 mg P m^{-2} d^{-1}), if overlying water SRP concentrations were initially low ($\leq$55 mg m^{-3}; this is low for Mendota during turnover). If initial overlying water SRP concentrations were higher (>100 mg m^{-3}, or representative of mean lake conditions after fall turnover), core SRP release rates were negligible or even negative (as low as -2.0 mg P m^{-2} d^{-1}). The sediments during the winter resting period had the capacity to remove P. Sediment IIP concentrations were also generally low (20 to 25 mg IIP m^{-3}) in the winter. Cores collected in late April and incubated aerobically at intermediate temperature (9.5°C) acted similarly to the winter cores. Moderate stirring of the overlying water decreased winter and spring core release rates (or even turned them negative) but accelerated summer oxic release rates.

Lake Wingra was similar to Lake Mendota except that the summer oxic release rates were much lower (2.5 to 3.0 mg P m^{-2} d^{-1}). Initial sediment IIP levels were also much lower (~29 mg m^{-3}) in these shallow (3.5 m) wind disturbed sediments. The IIP levels in the Lake Wingra incubated cores rose to 150 to 490 mg m^{-3} during the course of the incubations.

Specific weather factors probably influence the Wingra-Mendota release comparison. The Wingra sediments were gathered on 28 June 1974, following cold and windy May-June months. Conversely the Lake Mendota cores were obtained from 5.5 to 6 m water depth in mid July-mid August of 1973 and 1974. The wind energy drops off in these months, both in these and the normal years (Stauffer, 1980b), and 5 to 6 m is close to the breeze thermocline position. It is also worth noting that the Mendota release rates from July 1973 were threefold higher than July 1974. The warm summer of 1973 was noted for its high epilimnion PO_4 contents and algal standing crops following the extraordinarily high drainage basin export of P during the wet spring months and low April-May phytoplankton activity. It is thus apparent that greater over-lying water depth, warmer calmer antecedent conditions, and an accelerated organic deposition rate in the 1973 mid-summer period, could be contributing to an order of magnitude higher Mendota release rate as compared to Wingra release rate.

The non-calcareous lake sediment release rates of Holdren and Armstrong (1980) agree with Sonzogni et al. (1977) and Larsen et al. (1980) observations on Shagawa Lake, Minnesota and Mortimer's (1941; 1942) experience with Lakes Windermere and Eswaithe Water in the non-calcareous English Lake District. These Fe-rich sediments release negligible SRP under aerobic conditions.

The measurements of sediment P release by Holdren and Armstrong (1980) conform closely to expectations based on the previously discussed "mechanistic boundary layer model" involving sulfide inactivation of Fe(II). The model predicts high aerobic release rates for high antecedent organic carbon loading on the sediment, and high temperatures. These conditions correspond closely to the mid-summer measurements on Mendota (especially 1973). The importance of the invertebrates is that they increase the effective surface area of the sediment-water interface with their burrowing, while preserving the sulfide barrier near the channels necessary to immobilize Fe(II) and preserve SRP in solution once it encounters O_2. Goldhaber et al. (1977) have described sediment pyrite formation adjacent to the burrows of marine bio-turbated sediments with appreciable organic loadings. Bio-turbation perforates the sediment boundary and extends it, but preserves the sulfide microlayer "structure" of the sediment benthic boundary layer. Resuspension of sediments by violent stirring in the presence of O_2 indiscriminately destroys the sulfate reduction zones in the benthic boundary because the sulfate reducers are obligate anaerobes and are inhibited by such randomized perturbations of the sediment environment. Both the model and actual observation converge on the P release suppression effect of violent stirring. In strictly anoxic chambers stirring enhances SRP release because SRP retention in the overlying anoxic water does not depend on immobilizing Fe(II) as FeS. This explains Spear's (1970) anoxic experiments on Lake Mendota sediments, and is compatible with the experience of Mortimer (1941; 1942), who found that SRP was quickly precipitated (by oxidizing Fe(II)) if dissolved oxygen was let into a previously anoxic system.

The IIP measurements of Bannerman (1973) and Holdren and Armstrong (1980) during winter vs. summer are compatible with the sulfide inactivation model. Table 5 shows that during summer sulfide suppresses Fe(II) and ensures a low interstitial Fe/P ratio in calcareous lakes, but not the Fe-rich sulfide poor non-calcareous lakes. Serruya et al. (1974) made similar observations on calcareous Lake Kinneret; Emerson (1976) observed sulfide inactivation of Fe(II) in the Greifensee. The model applies to epilimnetic sediments under O_2-saturated overlying water if the organic sedimentation rate and sediment temperature are high enough.

In mid winter and early spring sediment-water relations suggest adsorption-desorption behavior of oxidized sediments. The winter sediment-release behavior of Mendota and Wingra sediments suggests a SRP "cross-over" concentration of 50 to 100 mg SRP m^{-3}. This is representative of equilibrium concentrations found both by Mayer and Gloss (1980) and Schroeder (1976). The implied low "cross-over" concentrations for the Fe-rich Northern Highlands lake sediments are consistent with the edaphic conditions in that nutrient-poor area.

Table 5. Fe/P Gradients in the Benthic Boundaries of Stratified Calcareous (C) vs. Non-Calcareous (N) Lakes.

Level* (cm)	Fe/P (Atomic) Greifenzee	(C)	Mendota	(C)	Minocqua	(N)
-2 to -35	0.06	E	0.04	S	19.4	S
+1	0.08	E	0.08	H	34.0	H
+3	0.56	E	0.17	H	34.0	H
+5	6.0	E	0.24	H	65.0	H
+45	63.0	E	--		--	

Notes:
* Zero at sediment-water interface; values increase downward into sediment.
E: Emerson (1976)
H: Holdren (1977)
S: Stauffer (unpublished)

F. Factor Interactions Among Lake Morphometry, Seasonal Stratification, Sediment-Water Interactions and Redox

1. Hypolimnetic Volume Development

The activity of the sediments in the internal phosphorus cycle of a lake depends on lake basin morphometry and the superimposed seasonal cycle of thermal stratification. One important measure is the ratio of main or storm thermocline depth to lake mean depth (Figure 15). If the lake is shallow and expansive (large fetch and A_o) and set in a windy climatic regime, then the potential thermocline depth may be deeper than the maximum lake depth. This is true of Lake Winnebago, Wisconsin (A_o = 55,730 hectares; z_{max} 6.4 m). In this situation (diagrammetrically shown in Figure 15A), the sediment-water interface everywhere has the temperature, pH, and redox condition of the mixed layer. Typically, this implies warm (22 to 25°C) alkaline (pH 8 to 10) aerobic conditions, a high organic carbon sedimentation rate (if the lake is productive) and release of sediment nutrients directly into the trophogenic layer.

As the lake progressively deepens, the main thermocline depth will form above the deep water sediments first as shown in Figure 15B, and finally as shown in Figure 15C. Clearly, as $\bar{z}$ increases, the distance from the sediment-water interface to the thermocline boundary increases, the hypolimnetic volume

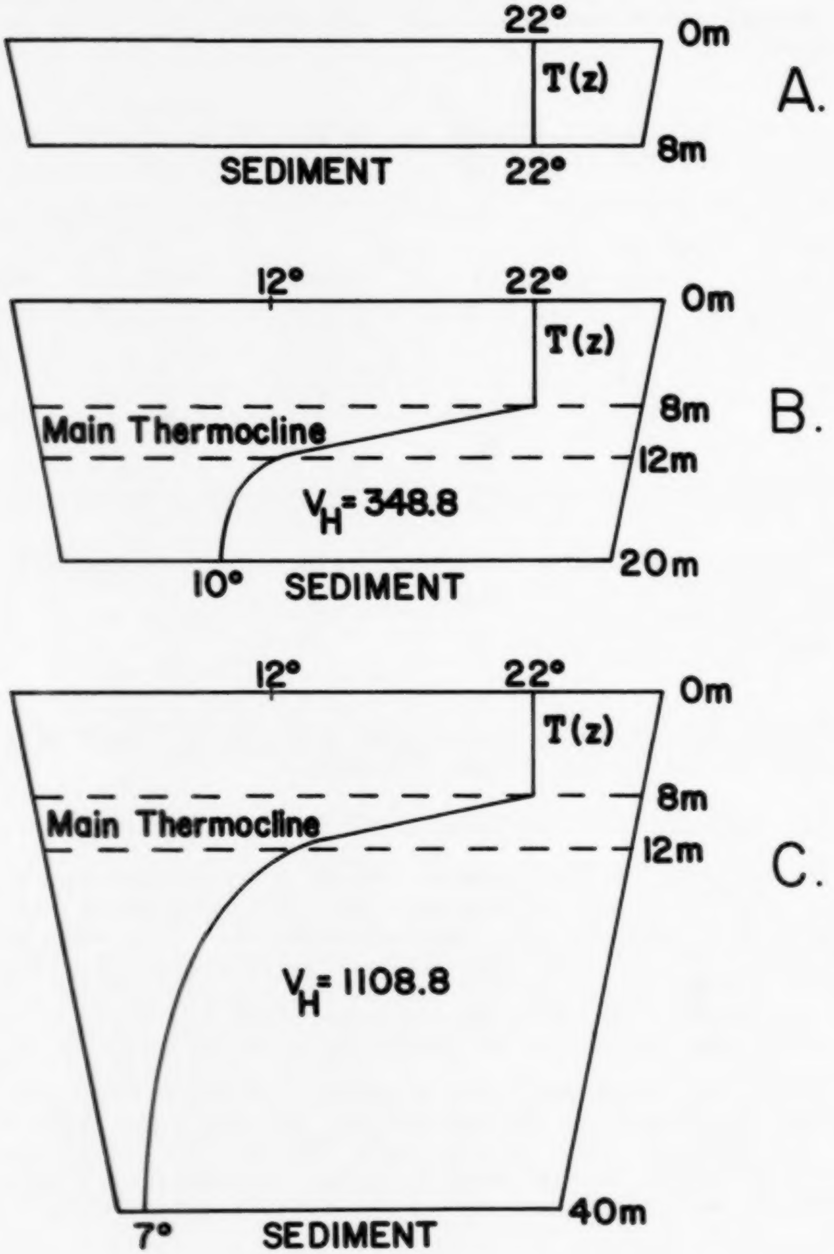
22°
0m
T(z)
A.
8m
SEDIMENT
22°
12°
22°
0m
T(z)
8m
B.
Main Thermocline
12m
V_H = 348.8
20m
10°
SEDIMENT
12°
22°
0m
T(z)
8m
Main Thermocline
12m
C.
V_H = 1108.8
40m
7°
SEDIMENT

Figure 15. Schematic cross sections for lakes.

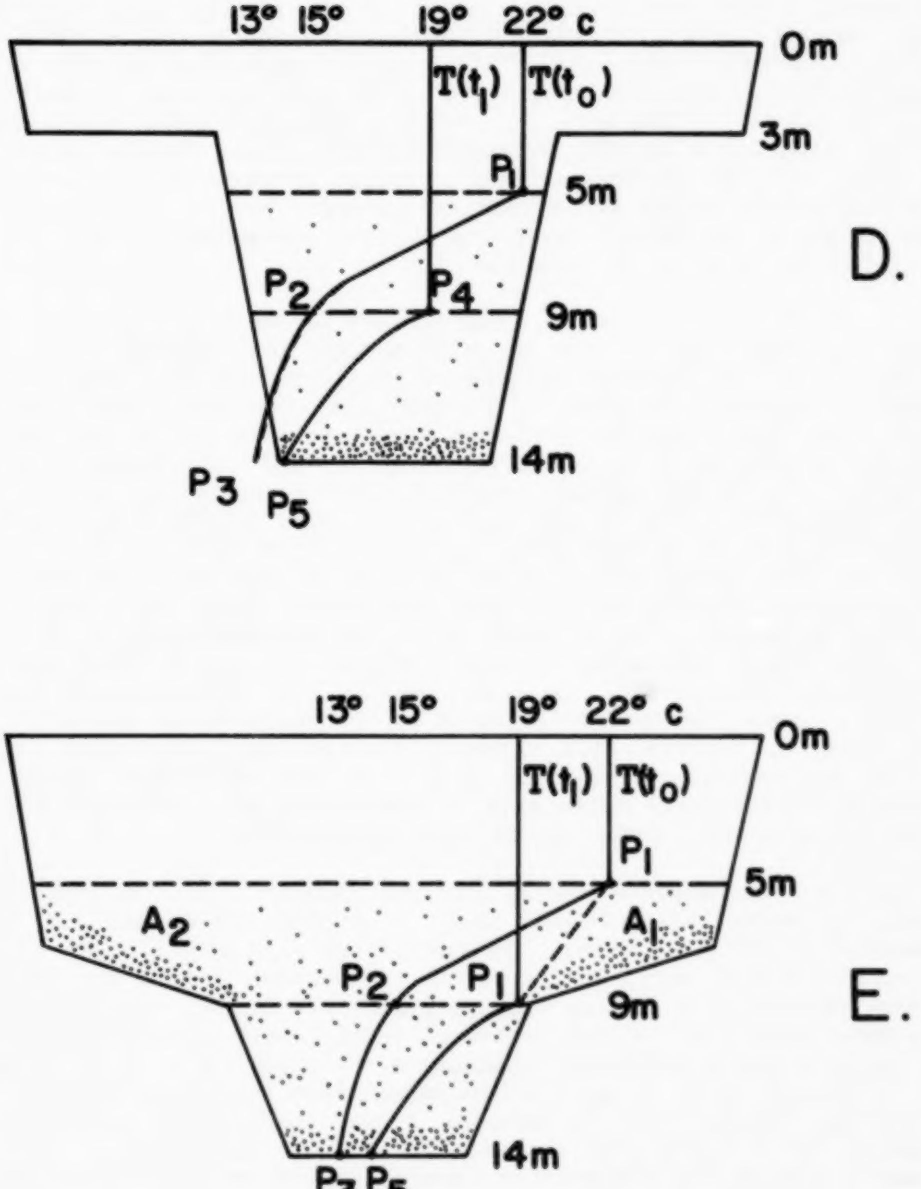
13° 15° 19° 22° c
0m
T(t1)
T(to)
3m
P1
5m
D.
P2
P4
9m
14m
P3
P5
13° 15° 19° 22° c
0m
T(t1)
T(to)
P1
5m
A2
A1
P2
P1
9m
E.
14m
P3
P5

Figure 15. (continued)

increases, and the temperature of the deep-water sediments decreases asymptotically to 4°C, both because of the delayed onset of the 4° isothermal condition after ice-out (see Section II-C), and because heat transported through the main thermocline is dispersed into a much larger water volume. The lower temperatures (closer to the 4° maximum density point for pure water), and decreasing temperature gradients ($\partial T/\partial z$) in the deeper lakes hypolimnion, imply low density stabilization of the deep hypolimnion and hence, enhanced rates of eddy diffusivity (Quay et al., 1980; Li, 1973; Stauffer, 1980hi). For Green Lake $\partial T/\partial z$ approaches $0.01°C\ m^{-1}$ and K_z increases by two orders of magnitude at 50 m as compared to the thermocline (Stauffer, 1980i). This enhanced vertical transport rate, coupled with lower sediment temperature and the increased initial oxygen storage (proportional to V_h), imply that the pelagic sediment surface of deep water lakes will remain aerobic even late in the stratification period. This will be true even if the productivity of the mixed layer and organic sedimentation rate are the same for all three scenarios (Figure 15A-C).

In the well-mixed scenario (Figure 15A) sediment release of P is enhanced by the high temperature, high pH, high organic sedimentation rate, biological utilization of P in the overlying water, and effective stirring rate above the sediment. However, as shown by Holdren and Armstrong (1980), and inferred from the sediment chemical exchange model proposed in Section II-E, aerobic sediment release of P is effective only for the calcareous lake or marine sediments. During the summer, immobilization of Fe(II) by sulfide results in a low Fe(II)/IIP ratio in the surface sediment interstitial water of these alkaline Fe-poor lake sediments, as shown by Holdren (1977) and Bannerman (1973) for the Yahara Chain lakes in Madison, and by J. Wiersma (personal communication, University of Wisconsin-Green Bay) for calcareous Lake Winnebago sediments. The periodicity in the windpower time series associated with cold fronts (Stauffer, 1980b) affects P release from shallow water sediments by interspersing low power periods with high power periods. During low power, concentrations of IIP build up in the surficial sediments; the high power acts to release this suddenly to the overlying water where it is utilized by the algal standing crop. In non-calcareous lakes the high interstitial Fe(II)/IIP ratio acts to immobilize the P accompanying transport and Fe(II) oxidation, and prior to algal utilization.

In the intermediate depth scenario (Figure 15B), aerobic sediment P release is potentially slower than in Figure 15A because of the colder temperature (~10°C). However, the restricted size of the hypolimnion implies that anoxia sets in early in the stratified period. During the anoxic period, sediment release of P is accelerated, especially for non-calcareous lakes. In calcareous lakes, the sulfide interception of Fe(II) again leads to a very low Fe/P ratio in the hypolimnion. Because of this low ratio, P is transported by eddy diffusion away from the sediment-water interface and up into the thermocline region. In the absence of Fe there is no important chemical mechanism for P reprecipitation even in the oxic metalimnion. The rate of P transport through the thermocline depends on the metalimnetic P gradient and the eddy diffusivity for solutes. The metalimnetic P gradient will be negligibly small if the euphotic zone overlaps the main thermocline. This happens in small calcareous seepage lakes and in Green Lake, Wisconsin in late summer (Stauffer, 1980hi). Non-calcareous lakes of intermediate depth accumulate P in the hypolimnion only after the onset of anoxia! Release of P (and Fe(II)) occurs at the anoxic sediment-water interface. These solutes migrate upward by eddy diffusion until dissolved oxygen is encountered. The oxygen oxidizes the Fe(II) and causes chemical reprecipitation of the P (see Section II-E).

In the deeper lakes hypolimnetic volume development is great enough so that this layer never goes completely anoxic (unless the lake is meromictic like the Black Sea). Sediment phosphorus release and storage in the oxic hypolimnion of a non-calcareous lake is never important. In calcareous Green Lake large quantities of both SRP and SiO_2 are released into the hypolimnion and stored until fall turn-over (Stauffer, 1980i).

2. Effects of Sediment Contact Area at Intermediate Depths

The scenarios in Figure 15A-C portray a steep sided lake with little sediment-water contact area until the flat floor of the pelagic basin is reached. Clearly, $\bar{z}/z_{max}$ is close to unity, and much larger than the ratio 0.5 or less found for most lakes. Large $\bar{z}$ and $\bar{z}/z_{max}$ values are typical of lakes occupying caldera and tectonic grabens (c.f. Hutchinson, 1957). Deep graben lakes (Lake Tahoe, California) and caldera lakes (Crater Lake, Oregon) are typically infertile because of the restricted drainage basins, and the remoteness of the deep-water sediments from the trophogenic layer. As the depth increases we have, in the limit, the one-dimensional model of the infertile tropical ocean. For shallower lakes with sediment "shelf" areas we must consider sediment contact area at the intermediate water depths.

Consider a partition of lake volume and associated sediment contact area accomplished by truncating horizontal planes positioned at integral meter (j) depths below the lake surface elevation. Define the ratio: $RA(j) = A_s(j)/A(j)$, as the sediment contact area divided by the lake area exactly j meters below the surface. Because the layers are exactly 1 m thick, RA(j) is also the ratio of sediment contact area to water volume for the jth element of the depth partition. Also, the inverse of RA(j) is the number of cubic meters of layer slice volume in contact with 1 m^2 sediment contact area. The RA(j) values are measures of potential sediment-water interactions for different lakes, and for different depth zones within the same lake. For a vertically sided lake the RA(j) ratios are zero until the flat bottom floor is reached, hence there is no influence of sediment contact area on the water chemistries of the intermediate layers.

Geologic processes (responsible for the origins of, and morphological changes in lake basins accompanying lake aging) lead to important typologies for the RA(j) vectors of many lakes. Two important morphological changes accompanying aging are the preferential development of the littoral sediment zone by shore reworking and macrophyte colonization, and the faster rate of sediment filling of the deep holes as compared to the pelagic slope sediments. As a result, RA(z) is typically moderately large for the shallower littoral zone, then drops off to a pronounced minimum at the intermediate lake depths, and finally increases exponentially to a maximum value exceeding 1.0 as z_{max} is approached. Of course, the RA(z) minimum is lower, and the depth range of this minimum broader, for lakes with large $\bar{z}$ and large $\bar{z}/z_{max}$ ratios.

One common depth-dependent pattern for glacial lakes is shown in Figure 16. All five lakes have a metalimnetic minimum in RA(z). Note the prominent littoral zone sediment contact area in Fish Lake, followed by the sharp drop in RA(z) at the intermediate lake depths. Green Lake (see also Figure 17) has notably low RA(z) values throughout the metalimnion and upper hypolimnion. The minimum ratio is 0.015 at 18 m; this implies 67 m^3 or volume for each m^2 sediment contact area at this depth. Furthermore, RA(z) does not increase again beyond 0.030 (the minimum RA(z) value for Lake Mendota, see also Figure 18) until a water depth of 45 m is reached. Lake Delavan is a conformal lake basin with larger amounts of sediment contact area at all depths (see Figure 19).

Unlike the typical conformal Wisconsin kettle lake left in thick glacial drift, or glacially dammed lakes in soft sedimentary strata (Green Lake, New York Finger Lakes), lakes in glacially sculptured hard rock drainage basins often have exceedingly complex, topographically aligned morphologies, including numerous islands, irregular shorelines, and irregular isolated deep holes. This complicates estimation of internal phosphorus supplies. Two examples are Shagawa and Burntside Lakes in NE Minnesota in the drainage of the Burntside River (Schults *et al*., 1976). Burntside Lake has at least seven isolated prominent deep holes; Shagawa Lake has three holes set in a profundal plane of 6-10 m overlying water depth. In vivid contrast to Lake Mendota, Shagawa Lake has a prominent RA(z) maximum at intermediate water depths (Figure 20). As suggested by Larsen *et al*. (1980) and shown by Stuaffer and Armstrong (1980b) this metalimnetic maximum is fundamental in regulating the magnitude and fate of internal phosphorus supplies in Shagawa Lake.

Employing the RA(z) values and pertinent data on sediment solute release rates, it is possible to calculate the *direct* potential effect of sediment release on the chemistry of each layer slice below the lake's surface. I call the effect "direct" because it depends on release and lateral dispersion *within* the layer slice and not on vertical transport (possibly impeded by density stabilization within the thermocline). If we assume, for example, the frequently observed anoxic sediment release rate of ~10 mg SRP m^{-2} d^{-1} (Holdren and Armstrong, 1980; Burns and Ross, 1972; Larsen *et al*., 1980), that release rate, continuing for a week, would raise the *average* P concentration at the 8 m level in Green, Mendota, Delavan, Fish, and the West Basin of Shagawa Lake by 1.3, 2.0, 7.8, 6.4, and 70.0 mg m^{-3}, respectively. We see that the release contribution of metalimnetic sediments is small in the two deepest lakes (Green, Mendota) but potentially huge in Shagawa Lake because of the extensive sediment shelf contact area at the 8 m level.

The above analysis assumed that phosphorus, once released, acted in a chemically conservative fashion (i.e., no biological uptake or chemical precipitation at the 8 m level). Furthermore, a chemical profile at the deep hole station would provide "average" layer phosphorus concentration only if lateral transport and dispersion instantaneously equalized the solute concentration everywhere within the layer slice. The first assumption

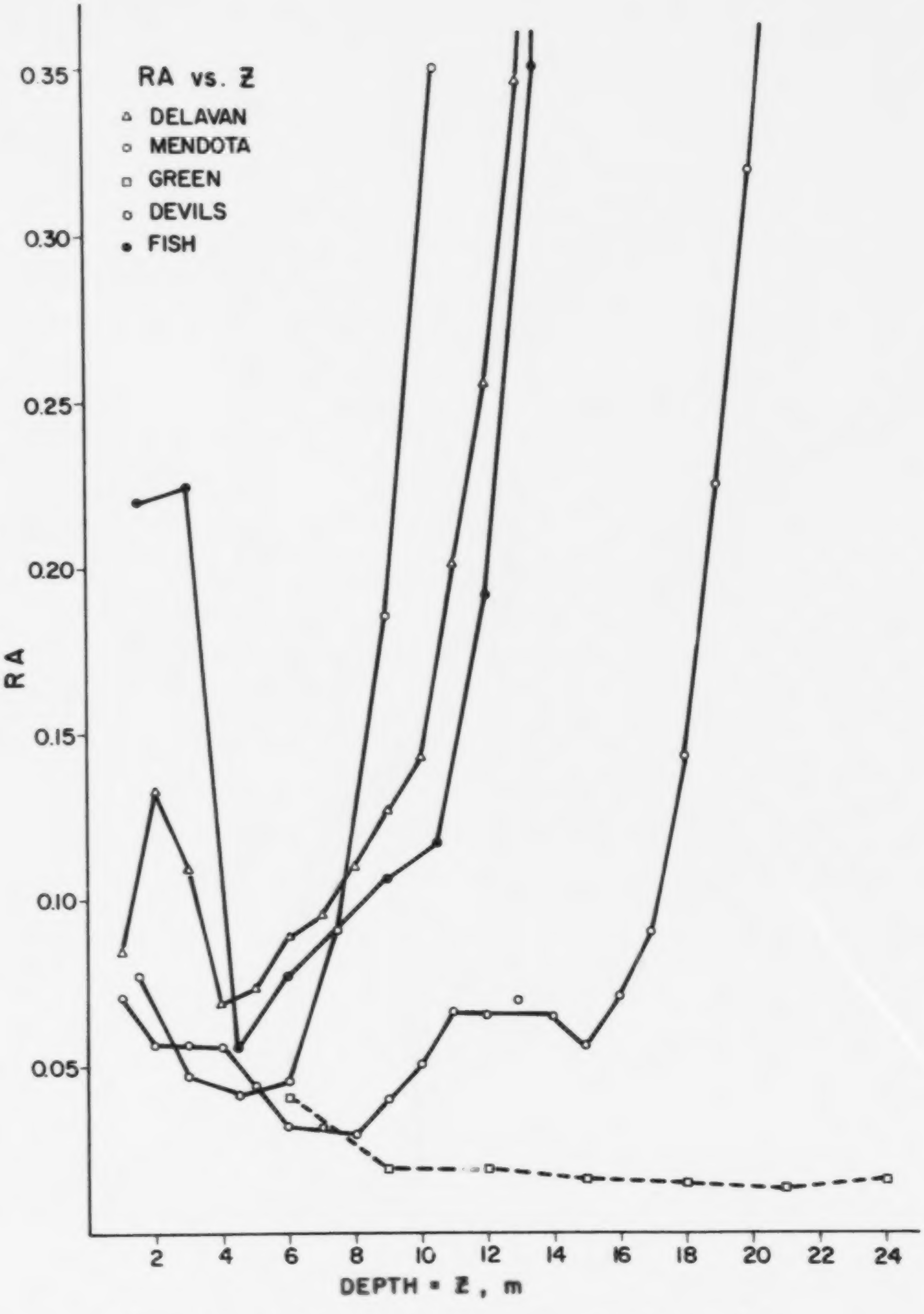

Figure 16. Ratio of sediment contact area to lake area for five southern Wisconsin lakes.

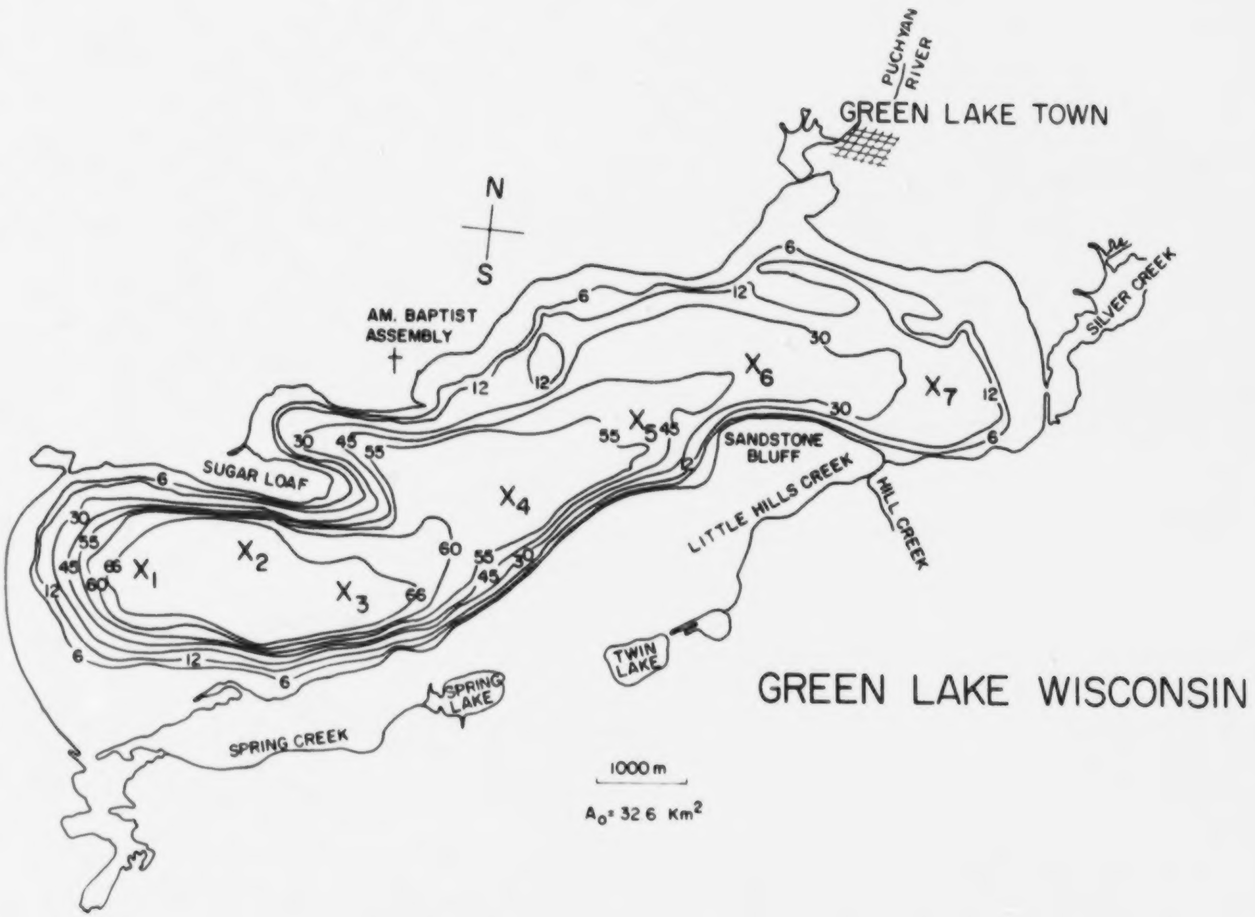
PUCHYAN RIVER
GREEN LAKE TOWN
N
S
AM. BAPTIST ASSEMBLY
SILVER CREEK
6
12
30
45
55
60
66
X_1
X_2
X_3
X_4
X_5
X_6
X_7
SUGAR LOAF
SANDSTONE BLUFF
LITTLE HILLS CREEK
HILL CREEK
TWIN LAKE
SPRING LAKE
SPRING CREEK
GREEN LAKE WISCONSIN
1000 m
$A_o = 32.6$ Km^2

Figure 17. Bathymetric map for Green Lake, Wisconsin.

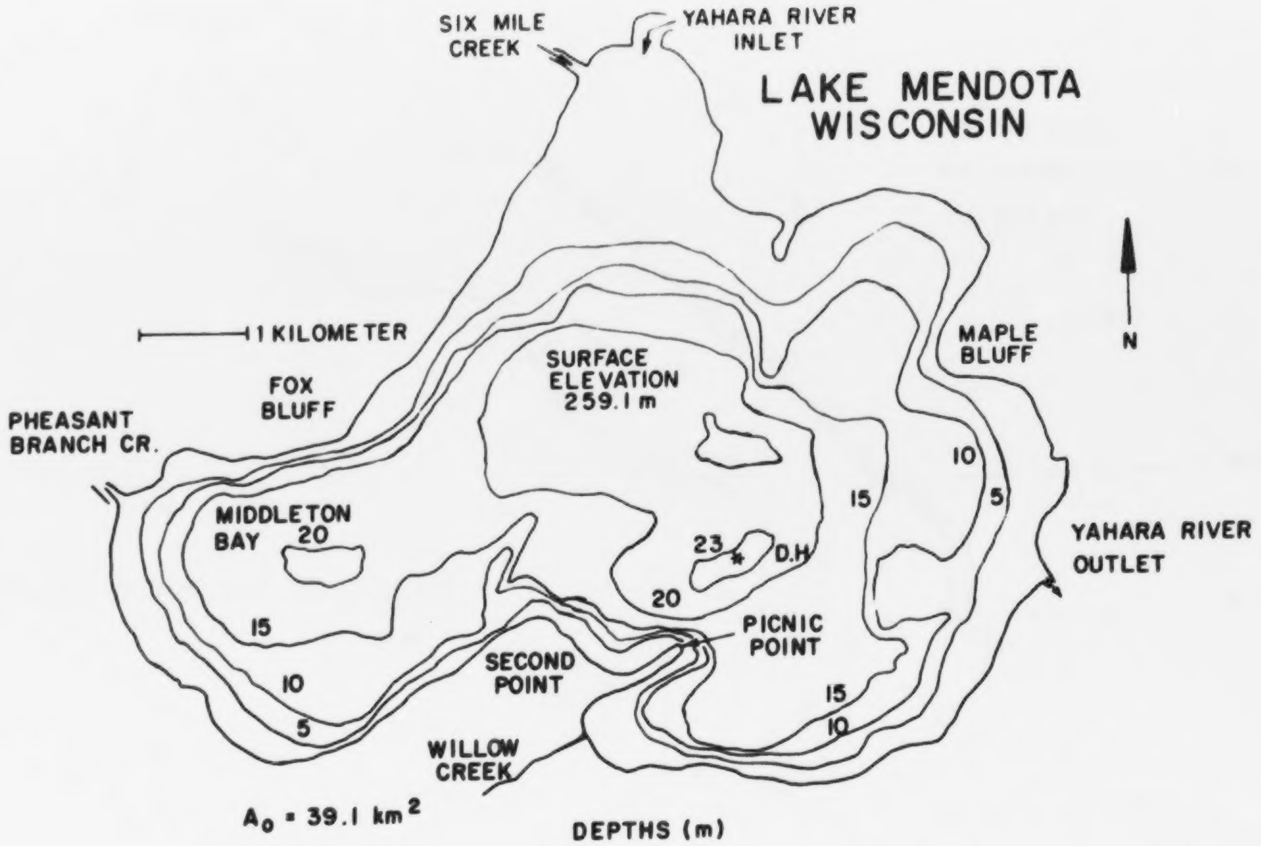
SIX MILE CREEK
YAHARA RIVER INLET
LAKE MENDOTA
WISCONSIN
N
1 KILOMETER
SURFACE ELEVATION 259.1 m
MAPLE BLUFF
FOX BLUFF
PHEASANT BRANCH CR.
MIDDLETON BAY
20
10
15
5
YAHARA RIVER OUTLET
23
D.H
20
PICNIC POINT
15
SECOND POINT
15
10
5
10
15
WILLOW CREEK
$A_0 = 39.1\ km^2$
DEPTHS (m)

Figure 18. Bathymetric map for Lake Mendota, Wisconsin.

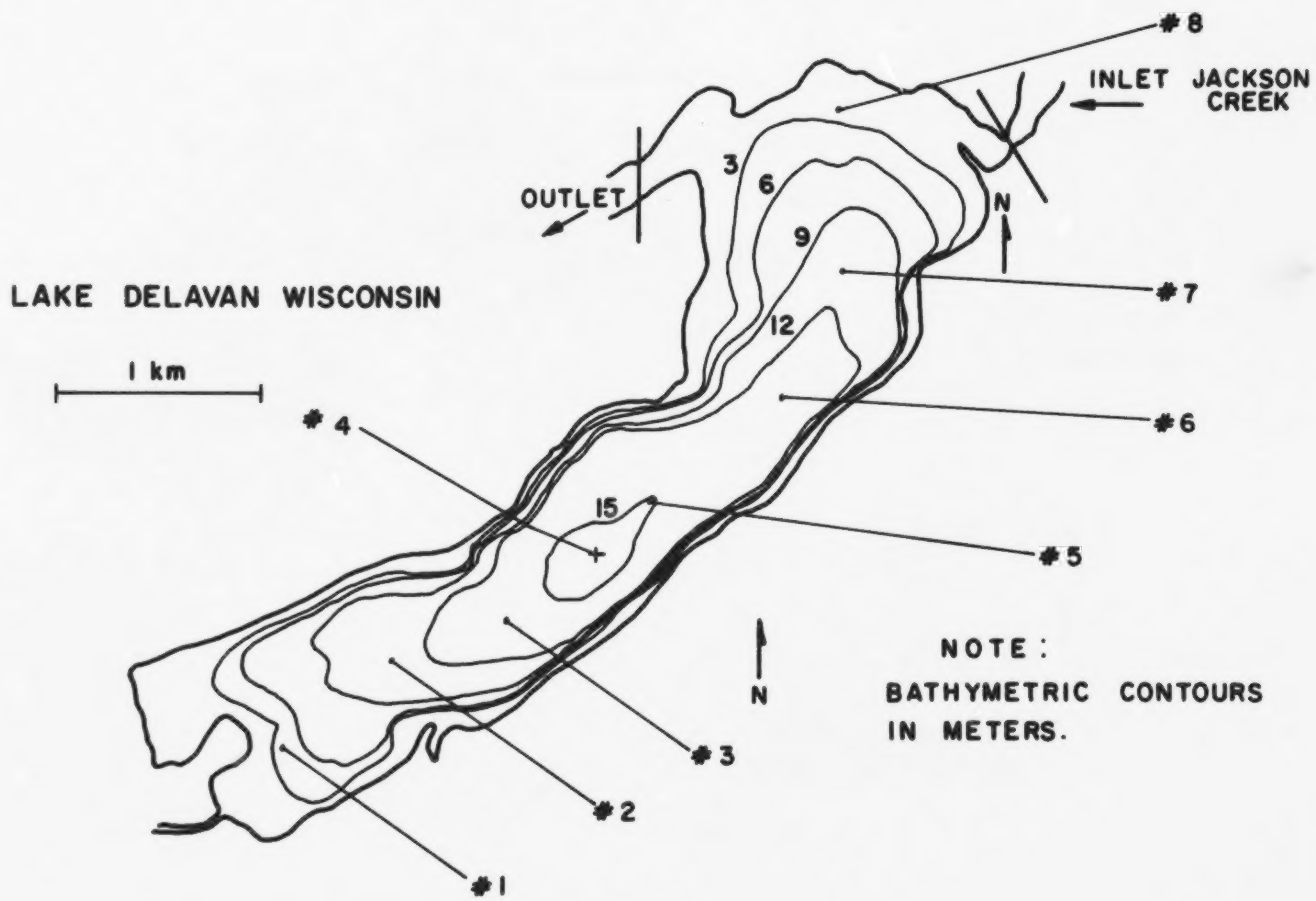
LAKE DELAVAN WISCONSIN
1 km
# 8
INLET JACKSON CREEK
OUTLET
N
3
6
9
12
15
# 7
# 6
# 5
# 4
# 3
# 2
# 1
N
NOTE:
BATHYMETRIC CONTOURS IN METERS.

Figure 19. Bathymetric map for Lake Delavan, Wisconsin.

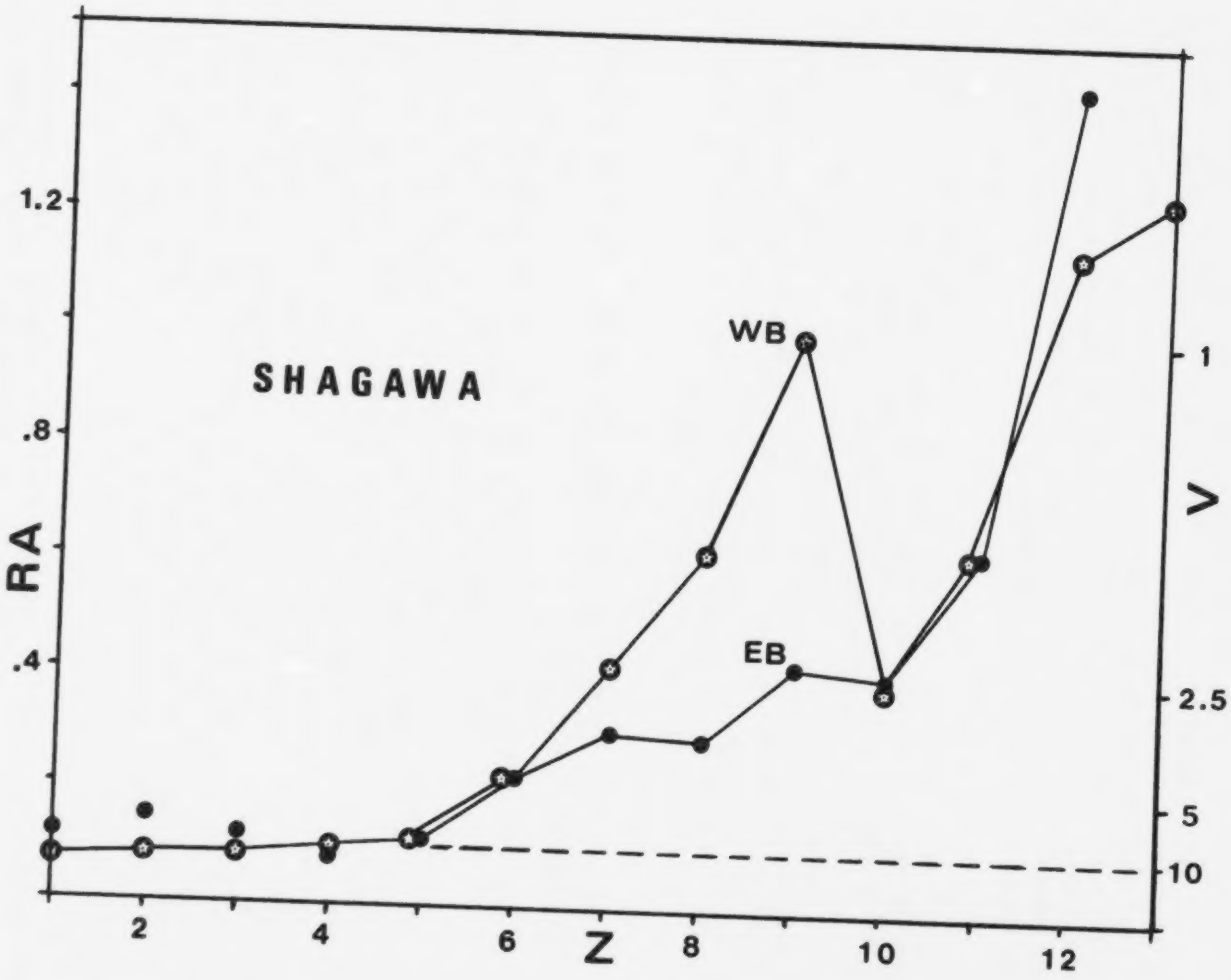

Figure 20. Ratio of sediment contact area to lake area for the east and west basins of Shagawa Lake, Minnestoa.

(conservatism) very nearly holds if: (1) the 8 m layer is deeper than the true depth of the euphotic layer, hence biological uptake to support photosynthesis is negligible (see Section II-D); (2) the atomic Fe/P sediment release ratio is significantly below 1.0 or the 8 m layer slice is everywhere anoxic. If this latter condition is violated, oxygen will be encountered during the lateral transport of P away from the anoxic sediment-water interface. At this contact, Fe(II) diffusing with the P will rapidly (minutes) oxidize to Fe(III) and immediately chemically bind the PO_4-P. The length of time required for this initially colloidal Fe(III)-bound phosphate to form a settlable precipitate increases (to days) as the ionic strength of the water decreases to values characteristic of non-calcareous lakes in northern Wisconsin, northern Minnesota and the Canadian shield region of Canada (Koenings, 1976; Koenings and Hooper, 1976; Stauffer and Armstrong, 1980a).

The multi-stage process defined by: (1) initial sediment Fe(II)/P release; (2) lateral diffusion away from the sediment shelf into deeper water; (3) Fe(II) oxidation in the oxygen enriched waters furthest from the sediment shelf; (4) Fe(III) binding to phosphate; and (5) coagulation and settling of the precipitate into deeper water; probably explains the very great enrichment of CDB or oxalate extractable Fe and P in non-calcareous stratified lakes of northern Wisconsin and Minnesota. Conversely, because the sediment Fe/P release ratio is very low in the calcareous lakes, the outlined multi-stage process for deep sediment enrichment is less effective for those two elements in calcareous lakes (Stauffer and Armstrong, 1980a).

3. Entrainment Transport of P Into the Mixed Layer Accompanying Thermocline Migration

Figures 15D and E illustrate lake cross sections where sediment "shelves" are present either in the epilimnion (3 m; scenario D) or within the metalimnion (7 to 9 m; scenario E). Scenario D corresponds most nearly to Fish Lake; here littoral zone sediment release of P and lateral transport into the pelagic zone is much more important than vertical transport of P through the thermocline during summer stratification (Stauffer, 1974; Erickson, 1980). The dominance of lateral transport from the littoral occurs because the littoral is extensive; vertical eddy diffusivity is very small ($\sim 10^{-3}$ cm^2 s^{-1}) within the geographically confined and highly stabilized thermocline of this small lake (A_o = 88 hectares), and because low epilimnetic total-P concentrations, low water color, and a shallow storm thermocline (~5 m) combine to allow the euphotic zone to completely overlap the metalimnion (Stauffer, 1974). Algal uptake of P in the metalimnion itself leads to low P vs. z gradients in the upper metalimnion (Stauffer, 1974). The net effect is a short circuiting of P directly into algae prior to its arrival in the mixed layer.

Scenario E corresponds to the West Basin of Shagawa Lake. Initially the mixed layer boundary (h_1) is at 5 m. A severe cold front sequence then deepens this to 9 m and cools the mean temperature of the epilimnion to ~19°C. Such mid-summer "events" have been described for the geographically extensive, wind-exposed West Basin by Larsen et al. (1980) and Stauffer and Armstrong

(1980b). Note that the large scale migration of the thermocline directly entrains the former metalimnion water, including the solute-enriched benthic boundary layer (~ 1 m thick) immediately above the shelf sediments (diagrammetrically: areas A_1 and A_2 in Figure 15E). In addition, following the usual pattern, heat is irreversibly added by eddy diffusion to the deeper waters of the basin ($z>9$ m) (c.f. Stauffer and Lee, 1973; Stauffer, 1980h; Stauffer and Armstrong, 1980b for more detailed discussion).

Following the cold front, rewarming of the mixed layer occurs during the low wind power interlude, a new thermocline is set up above the 5 m plane, and the former metalimnetic shelf is again hydraulically partitioned off from the mixed layer. However, because of the higher water temperatures and very high RA(z) ratios (~1.0 for Shagawa West Basin metalimnion), oxygen depletion of the 7-9 m stratum proceeds rapidly and again triggers the release of sediment-P. If this release period is long enough, the next episode of thermocline deepening again entrains phosphorus rich water into a mixed layer (Stauffer and Armstrong, 1980b). In non-calcareous Shagawa Lake profile sampling the deep holes fails to estimate the water column P "storage" in the vicinity of the extensive shelf.

The situation in Lakes Mendota and Delavan is substantially different. In these "sulfuretum" lakes the upper metalimnetic phosphorus gradient exceeds 100 mg SRP m^{-4} by late summer, irrespective of oxygen concentration in the upper metalimnion! Furthermore, very active migration of the thermocline and eddy diffusion through the middle of the metalimnion transports large quantities of NH_3-N and SRP in both lakes during the summer stratification period (Stauffer and Lee, 1973; Stauffer, 1974; Stauffer, 1980h). Both morphometric and chemical differences between these two eutrophic calcareous lakes, and non-calcareous Shagawa Lake, de-emphasize metalimnetic contact sediments in the two calcareous lakes. In Shagawa Lake they are critical (Stauffer, 1980h; Stauffer and Armstrong, 1980b).

III. Estimation

A. Sampling Equipment

By connecting the intake tube of a peristaltic pump to an underwater conductance-thermistor probe, lake water samples can be easily obtained from thin (~5 cm) depth strata in the thermocline region and even in close proximity to the sediment-water interface. Filtered sample splits can be obtained on-station without air contacting the sample. The probe identifies the *in situ* sample temperature to within ±0.01°C and the conductance to ±1 μmhos. The temperature covariate is essential for accurate descriptions of solute transport processes in stratified lakes. The conductance can be used as a solute covariate for rapid exploratory surveys of lake sediment shelf areas (see later discussion).

A portable "Masterflex" peristaltic sampling pump (Horizon Ecology Co., Chicago, IL) is fitted with a Model 7015 pump head and silicone tubing. The inlet tube of the pump-head is serially connected to 50' sections of Tygon tubing (manufacturer recommendation, ID = 0.1925", OD = .3915"). The requisite number of sections depends on the desired sampling depth. The inlet end of the Tygon sampling tube is connected to a stainless steel flow-through weight (Horizon Co.), which is taped to the conductance-thermistor probe of a Whitney precision electronic conductance thermometer (Figure 21). The Whitney cable is used for depth referencing. The pump's outlet tube is conveniently connected via a T, plug and needle valves, Swagelok fittings, and Teflon connecting tube, to a Nucleopore 57 mm Swin-Lok pressure filter apparatus, to allow collection of a filtered (0.4 µm pore size) sample split within seconds of collecting the unfiltered split, and without the water sample ever contacting the air. The valves are used for controlling pressure across the filter. Customized large diameter pressure-filter assemblies are required for large sample sizes (>250 ml, Ball et al. 1976).

The pump is rated at 700 ml min^{-1} when fully charged and without the added impedance of the pressure filter assembly. From the dead-volume of the tubing (18.8 ml m^{-1}), the calculated water transit delay is 1.64 s m^{-1}. The calculated intake velocity at the two 7 mm orifices in the flow-through weight is 15.2 cm s^{-1}. Assuming a cone-shaped flow field with angle $\alpha=90°$ extending away from the intake orifices, the calculated mean velocity through the cone's base, 5 cm from the orifice drops to 0.1 cm s^{-1} (Figure 21). This value is an order of magnitude lower than typical hypolimnetic bottom currents in Lake Mendota (John Colman, Water Chemistry Laboratory, UW-Madison, personal communication).

The Whitney thermometer probe precisely estimates in situ water temperature at the probe orifice. The accuracy is improved by considering the time delay for water transit through the tubing. The highly accurate and precise estimates of sample in situ temperature find utility in estimating hypolimnetic solute concentration gradients in the presence of isotherm tilts, and in estimating eddy diffusion transport in stratified lakes (Sweers, 1970).

The accuracy and precision of the z sample coordinate depends both on the boat being securely anchored, and also on the surface roughness. Under optimal weather conditions the variance in z is likely to be ~1 cm^2 for the ~30 seconds required to collect a 250 ml unfiltered sample at any predetermined depth. Because the intake orifices of the flow-through sampling weight generates a flow field whose axis is orthogonal to z (Figure 21), the sample is obtained from a thin water slice. The vertical thickness of the slice depends on the temperature (hence density) gradient at level z, in accordance with the Richardson number characterizing laminar or turbulent flows in density stratified fluids. I have routinely obtained perfectly clear pump samples from within 5-10 cm of the sediment-water interface of Lake Mendota in overlying water depths of 24 m.

An important asset of the described procedure is the ability to obtain either filtered or unfiltered sample splits without transfer steps and without the sample contacting the air. This capability is necessary in chemical studies of iron, manganese, phosphorus, arsenic and sulfur in the bottom boundary layer. Heaney and Davision (1977) and Stauffer and Armstrong (1980a) have emphasized the importance of sampling procedures in studying redox-sensitive chemical species.

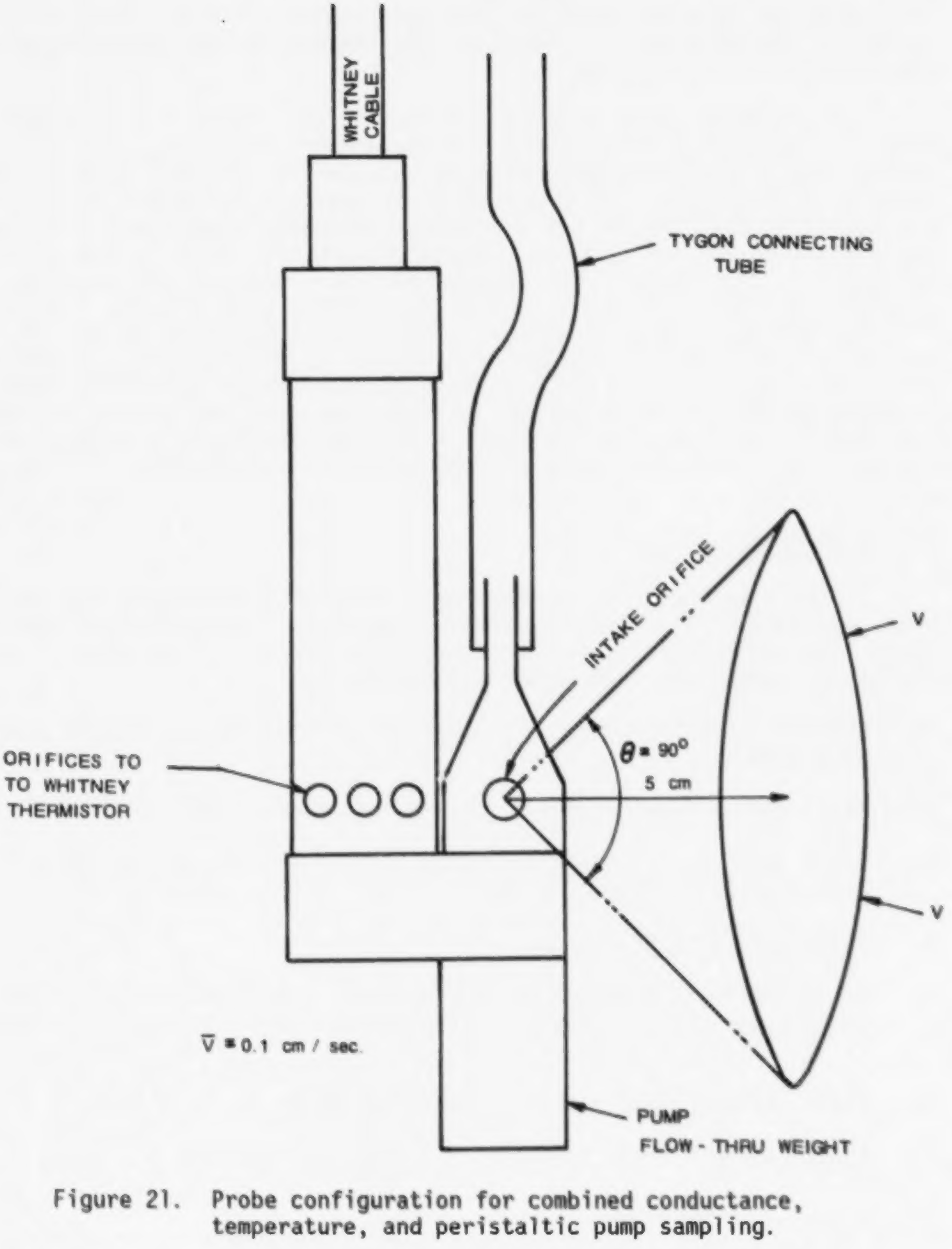
WHITNEY CABLE
TYGON CONNECTING TUBE
INTAKE ORIFICE
V
V
θ = 90°
5 cm
ORIFICES TO TO WHITNEY THERMISTOR
$\overline{V}$ = 0.1 cm / sec.
PUMP FLOW - THRU WEIGHT

Figure 21. Probe configuration for combined conductance, temperature, and peristaltic pump sampling.

The described procedure is also costwise more efficient than the use of Van Dorn and other messenger-tripped bottle samplers. Thus, on the first day of testing an aggregate 48 samples were obtained from six stations in Lake Mendota in approximately 3½ hours, including boat travel time. Only one person is required for the sampling. All but five of these samples were taken from below the 12 m thermocline. For sampling at the 30 m depth approximately 1 min per 250 ml sample is required; the temperature and conductance profiles are obtained simultaneously.

The procedure works equally well during the winter. Only a small auger hole is required for inserting the electronic probe-tube assembly and the Whitney cable can be securely clamped to a 2x4" or aluminum strut to preserve "down-hole" position. In this way it is possible to obtain detailed solute concentration profiles in the 1 m benthic boundary layer where concentrations are increasing exponentially with depth (Figure 22). This is impossible using conventional "Van Dorn" type sample bottles. Use of the pressure filter assembly on the outlet tube of the peristaltic pump allows collection of a filtered sample split as in summer. If the air temperature is much below 0°C, the tubes should be dry before first setting up in the field. Otherwise, ice formation will plug the tubes. Because the lake water "down-hole" temperature is usually 2°C, water drawn up by the pump will not freeze in the tubes provided the pump is left running! A 12 volt lead-acid car battery should be brought along for ensured electric power during cold weather.

B. Analytical Methods

The lake manager must be thoroughly acquainted with analytical methods if s/he expects to obtain useful physical-chemical information on lake trophic state and external and internal nutrient fluxes and storage. Important classes of parameters include the following:

1. General physical-chemical "Master Variables": Temperature, pH, dissolved O_2
2. Major cation-anion balance: Ca, Mg, Na, K, carbonate alkalinity; SO_4, Cl
3. Redox sensitive transition metals acting as "Master Variables" in the lake chemical system: Fe, Mn
4. Dissolved sulfide
5. Macro-nutrients frequently biologically limiting (c.f. Verhoff, 1973; Gerhart and Likens, 1975 for discussion of limiting nutrient concept); N, P, Si
6. Algal standing crop variable: chlorophyll a
7. Ionic strength proxy variable: in situ conductance.

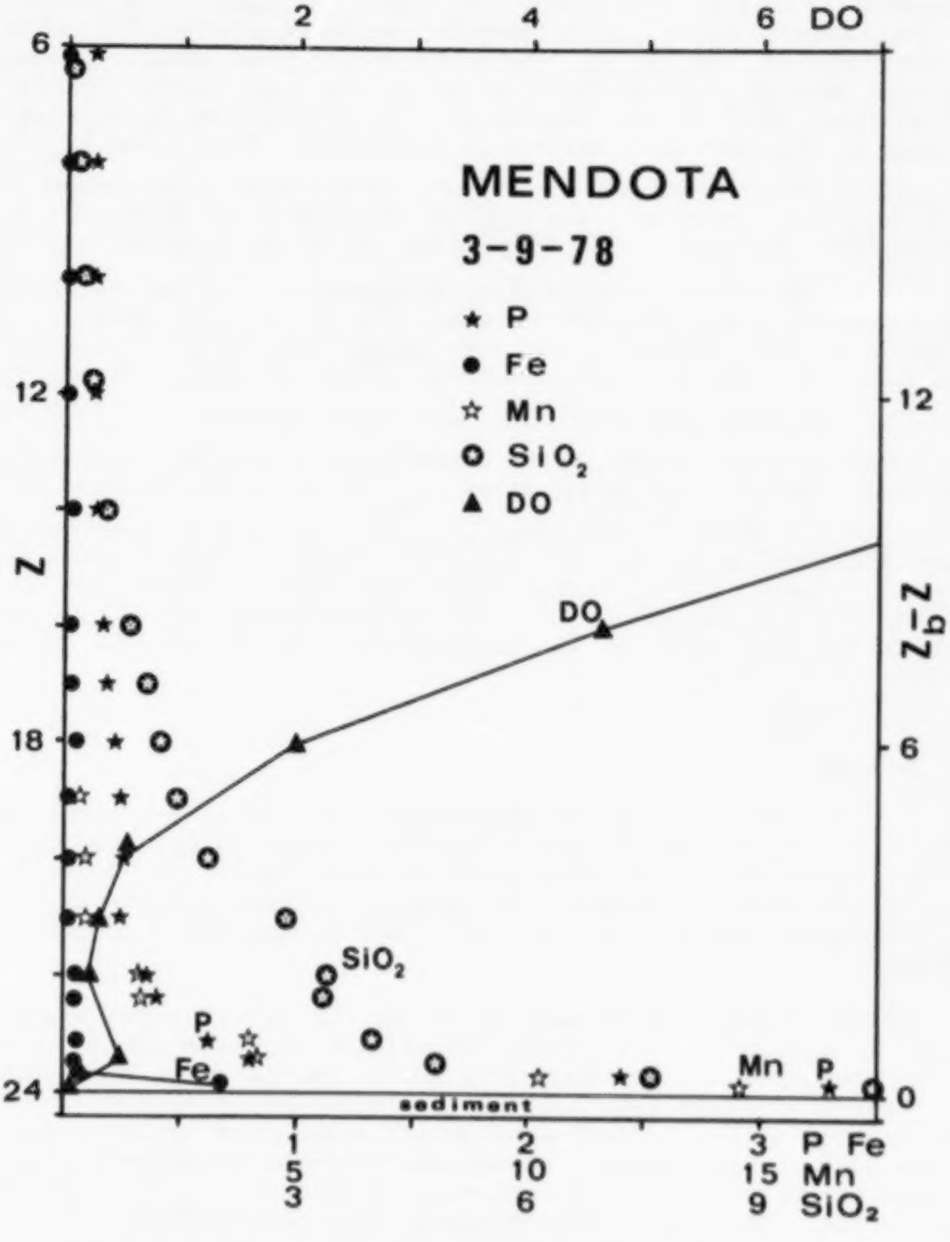

Figure 22. Solute concentration profiles for Lake Mendota, March 9, 1978.

1. Temperature.

Accurate and precise temperature data are essential for defining the progress of thermal stratification, and for calculating inter-layer fluxes of heat and solutes using the "flux-gradient" algorithm (Section III-D). Lake temperature is obtained using an electronic *in situ* thermometer probe (3-element thermistor or platinum wire resistance type). The errors depend on the instrument's *consistent* calibration against precision NBS references and on the inherent *quality* of the electronics. The requisite accuracy and precision depends both on the lake and on the time interval over which eddy diffusivities have to be calculated. In general, analytical quality must increase as the lake gets smaller (A_o) and deeper (both z and z_{max}/z), and as the time interval shortens. For lakes with medium areal extent and medium depth (example: Mendota), the *minimum* acceptable accuracy and precision is $\sigma_a = \pm 0.05°C$ throughout the temperature range of interest *and* over the duration of the summer stratification measurements. During the dynamic spring heating period lesser instrumental capability is required, however, this early period is of less interest to the lake manager interested in internal nutrient supplies. For smaller lakes (maximum fetch $\lesssim 2$ km) with $z_{max} \gtrsim 15$ m, the requisite accuracy and precision must each improve to $\sigma_a = 0.01°C$. The "Montedoro Whitney" company sells thermometers attaining these high standards (Stauffer, 1980hi). For deeper lakes ($z_{max} > 35$ m) in the medium size range (10 to 100 km²) a ±0.01 °C instrumental capability is also required during the summer stationarity period (c.f. Stauffer, 1980hi). Table 6 shows the monthly rates of summer heating of the lower hypolimnetic waters, and the minimum hypolimnetic temperature gradient for representative lakes in Wisconsin. The Table gives some idea of the temperature "signal" you are attempting to measure.

2. pH

Accurate pH data from the metalimnion-hypolimnion are useful for interpreting the Ca, Fe, Mn, S, and P cycles in lakes. Unless the lake is acidic and dystrophic (c.f. Hutchinson, 1957) pH data from the epilimnion has limited utility (it usually reflects the *temporal* balance between CO_2 uptake for photosynthesis, respiration, and CO_2 invasion from the atmosphere (Emerson, 1975ab).

pH measurements are recommended in the thermocline region where dissolved oxygen is approaching zero (solute oxidation-P adsorption zone), in the middle of the hypolimnion, and especially 25 to 50 cm above the sediment-water interface in the deep hole region. The latter measurement yields pH information relevant to the sediment-water solute release and sulfate reduction zone. If the lake is significantly bicarbonate-buffered, these pH measurements can be expected to fall in the narrow range, 6.75 to 7.6, late in the stratification period. The deep benthic boundary layer experiencing sulfate reduction normally has a narrower pH range (7.1 to 7.5; Stauffer and Armstrong, 1980a; Davison and Heaney, 1978).

Table 6. Mid Summer Hypolimnetic Heating Rates and Temeprature Gradients in Representative Wisconsin Lakes.

	Lake	Date Period	Morphometric Data						
			A_o km²	$\bar{Z}$ (m)	Z_{max} (m)	Z* (m)	$T(z,t_o)$*	Heating† Rate	Temperature‡ Gradient
1.	Trout-N	8/5/78-8/25/78	5.2	14.6	28	23	7.21	0.31	0.06
2.	Trout-S	8/5/78-8/25/78	10.7	13.4	35	30	6.65	0.25	0.05
3.	Mendota	7/7/79-9/12/79	39.1	12.4	24	20	10.92	0.63	0.23
4.	Monona	7/3/78-9/18/78	12.6	8.2	19	15	12.15	0.34	0.28
5.	Green	7/10/78-9/10/78	32.6	31.0	67	62	5.41	0.02	0.015
6.	Fish	5/26/72-9/3/72	0.88	6.0	17	15	5.70	0.20	0.07

* Initial temperature at depth z.

† Units: cal mL^{-1} $month^{-1}$ (°C $month^{-1}$).

‡ °C m^{-1}.

The following procedure is capable of providing in situ pH estimates accurate within ±0.05 pH unit. The actual pH measurements should be made in the laboratory on field preserved samples (see below). The field procedures used for obtaining and preserving the samples are critical if accurate in situ values are to be expected. Unwanted oxidation of redox sensitive solutes (Mn(II), Fe(II), H_2S) lowers the pH, while gas exchange with the atmosphere (esp. CO_2 and H_2S) has the effect of raising the pH. Fortunately, these changes can be avoided.

Collect the pH samples using Pyrex "Winkler" D.O. bottles and a peristaltic pump. Flush the bottle by overflowing several bottle volumes with sample by holding the outflow tube (bypass the filter) orifice near the bottom of the Winkler bottle. Slowly withdraw the tube, thus filling the bottle neck; then immediately seal the bottle with the ground glass stopper. Secure the stopper with glass-tape. Place the bottle in an iced darkened cooler and leave refrigerated until just prior to the laboratory-based pH determination. Begin the laboratory portion of the analysis as soon as practical (within a few hours).

In the laboratory allow the samples to warm to room temperature, while remaining tightly stoppered in the dark. Select suitably dilute reference buffers (near pH 7) that narrowly span the expected pH range. Acclimate the buffers to the same known laboratory temperature (preferably 20 to 25°C to improve electrode response). After calibrating the high quality glass pH electrode in the buffers, condition it for a few minutes in a sample of the lake's epilimnion water (approximately same ionic strength as hypolimnion samples) before making the pH determinations on the deeper water samples. Finally, determine the pH (at lab temperature) of the deeper water samples by inserting the pH electrode immediately after removing the glass stopper seal. The electrode will nearly fill the hole and come to equilibrium before significant gas exchange or oxidation can take place. Back calculate the in situ pH at the in situ temperature for the bicarbonate system following Davison and Heaney (1978).

Field in situ direct pH measurments are not recommended for all of the following reasons: (1) High quality pH instrumentation is easily damaged in the field; (2) it is difficult to bring buffers and water samples to a common temperature in the field; (3) the pH electrode responds sluggishly and sometimes erratically at low temperatures, hence an accurate buffer calibration is difficult; (4) if pH measurements are attempted in a "flow-thru" cell connected to the peristaltic pump's outflow tube, additional problems (in addition to (2), (3) above) are encountered with water "streaming potential" and/or pH shifts accompanying sample oxidation or degassing; and (5) winter field measurements add impossible further complications; such measuremnts are important and yet no more difficult to make using the bottle preservation-laboratory technique outlined here.

3. Dissolved Oxygen (D.O.)

Standard procedures are adequate except for D.O. concentrations <0.2 mg L^{-1}. The potentiometric in situ measurements are easily obtained and of requisite accuracy and precision, provided the instrument is accurately calibrated. Winkler titrations are also acceptable (c.f. APHA, 1971).

4. Major Cations

Flame atomic absorption spectrometry should be used on HCl-acidified sample splits (see below) following standard procedures. The analytical coefficient of variation $c.v._a \simeq \pm 1\%$.

5. Bicarbonate Alkalinity

For moderately well-buffered typical lake waters (alk.>0.5 mN) with low borate and ammonia concentrations, standard acid titration suffices (APHA, 1971). Depending on the initial pH, borate, NH_3, and even silicate can add acid titration alkalinity, however, this is rarely a problem except for geothermal waters at high pH. For poorly buffered natural waters, and especially for highly colored lake and stream waters, accurate carbonate alkalinity measurements are very difficult for the inexperienced analyst. Hire a chemical consultant.

6. Sulfate and Chloride

For most situations the "cation exchange" method is by far the best SO_4 technique from the standpoint of cost and low analytical error. See Stainton (1974) and especially Stauffer (1980g) for a careful analysis of the potential analytical biases and optimal analytical strategies. Note that sulfide present in a natural water sample can be bacteriologically oxidized to SO_4 if allowed to stand. Chloride is readily determined either by standard "Mohr" titration (APHA, 1971) or by "cation exchange" (Stainton, 1974; Stauffer, 1980g).

7. Iron and Manganese

These elements exist both as oxidized (Fe(III) and Mn (IV)) particulate phases and as reduced dissolved species under low redox conditions (Fe(II) and Mn (II)). Several analytical techniques are available for the direct determination of the "reduced" forms of these elements (c.f. Delfino and Lee (1969); Davison (1977); Shapiro (1966); Lee and Stumm (1960)). However, from the perspective of the lake manager or consultant it usually suffices to know both the total and total dissolved concentration. These are readily obtained by flame atomic absorption spectrometry on FA (field filtered and acidified) or UA (unfiltered acidified) sample splits. Low concentrations can be determined following the complexation-solvent extraction scheme of Kennedy and Zellweger (1973). Kennedy and Zellweger (1974) note that 0.4 µm pore size filtrates seriously overestimate the true "dissolved" Fe and Mn components in natural waters of high redox potential. This analytical bias is not a problem in the anoxic hypolimnion waters; here the filtered acidified sample split estimates Mn(II) and Fe(II) in the environment.

8. Dissolved Sulfide

Outlined below is a modified ZnS-iodine-thiosulfate technique based on a standard procedure (APHA, 1971). For hypolimnetic waters with relatively high concentrations of dissolved sulfite ($\gtrsim 0.5$ mg L^{-1}, and preferably greater), collect a 250 ml sample as for D.O. analysis using a peristaltic pump and immediately "fix" the sulfide by adding zinc acetate (c.f. APHA, 1971). The precipitated ZnS is later quantitatively recovered on a glass fiber filter in the laboratory and the filter reacted with an excess of standardized iodine in acid medium. Finally, the excess iodine is titrated with standard thiosulfate. Iodine consuming organics in the precipitate can give an important positive interference, especially for colored Fe-rich non-calcareous waters where the dissolved sulfide concentration is low. The technique works especially well for calcareous "sulfuretums".

The ZnS precipitate formed above can also be solubilized using an alkaline-ascorbic acid anti-oxidant buffer and the sulfide determined potentiometrically using a sulfide-specific electrode (Baumann, 1974). Other useful techniques have been developed by Cline (1969) and Davison (1977). The latter is good for low concentrations of sulfide but requires specialized polarographic equipment.

9. Nutrients: N:P:Si

Inorganic nitrogen is generally present in the form of ammonia (NH_3-N) or nitrate (NO_3-N). Nitrite is rarely present in significant concentrations relative to the other two forms. Ammonia is readily determined at environmental levels (and especially within the hypolimnion) using the popular phenol-hypochlorite colorimetric procedure which has been adapted to autoanalyzers (Strickland and Parsons, 1968). The NO_3-N concentrations encountered in stream flow in sedimentary regions, and over winter in lakes, can be determined using the brucine procedure (Kahn and Brezinski, 1967). Low nitrate levels require a reduction step (Cadmium column, for example) to nitrite followed by diazotization (Strickland and Parsons, 1968).

Soluble reactive phosphorus (abbreviated SRP) determinations are based on the ascorbic acid reduction molybdenum-blue procedure (Murphy and Riley, 1962; see also Strickland and Parsons, 1968 for a popular variant). Very low SRP concentrations can be determined following Stephens (1963). Total-P and total soluble P (TSP) fractions are determined colorimetrically in the same fashion after first liberating organically bound P by persulfate digestion in an autoclave (Menzel and Corwin, 1965). The particulate-P fraction can be determined indirectly by arithmetic difference, or preferably, directly by digesting particulates caught on a 0.4 nm nucleopore filter (Erickson, 1980). A high quality spectrophotometer equipped with 5 cm cuvettes is required for most environmental P determinations.

The phosphorus analytical procedure is less straightforward than commonly supposed. As a result, environmental P data can be analytically biased by hundreds and even thousands of percent. Arsenic present as arsenate (As(V)) reacts with molybdenum to give a positive interference (Johnson and Pilson, 1972; Stauffer, 1980e). The lake management consultant must verify whether or not arsenic is a potential analytical interference in the study lake because arsenic levels have been elevated in many Midwestern lakes from long histories of sodium arsenite treatments for weed control.

Silica is also an insidious potential P interference because of the very high Si/P ratios in many P-poor natural waters. Silica forms a positive colorimetric interference if the H^+ and H^+/Mo ratios are too low (as for example, specified by Strickland and Parsons (1968)); and/or the color is developed at elevated temperature in an auto-analyzer variant of the basic procedure (see Stauffer, 1980ef; 1980f for details).

Reactive silica concentrations are readily determined following the Fanning and Pilson (1973) refinement of the Mullin and Riley (1955) colorimetric procedure (c.f. Strickland and Parsons, 1968).

10. Chlorophyll *a*

Chlorophyll *a* is determined by solvent extraction of algal cells caught on a glass fiber filter. See Stauffer *et al*. (1979) for a streamlined procedure and discussion of potential extraction biases using acetone (90%).

11. Conductance

Edmondson (1956) introduced the useful procedure of measuring conductivity *in situ*. Modern high quality combination temperature-conductance instruments (for example, Montedoro Whitney Model CTU4) are highly accurate and precise. Frequently, the *in situ* conductance is adjusted to a temperature of 25°C based on the measured *in situ* temperature and the known conductance properties of *NaCl* solutions. For low temperatures, the differential ion mobilities (with respect to temperature shifts) cause a small but consistent bias for calcium bicarbonate lake waters.

12. Sample Preservation in the Field

Both filtered and unfiltered sample splits should be acidified with 1 ml conc. HCl/250 ml sample in the field for analysis of major cations, Mn, Fe, and nutrients. Hydrochloric acid is the ideal acid for this purpose because it causes no later analytical interferences. The acid prevents biological uptake of nutrients, sorption on the walls of the polyethylene sampling bottles (Heron, 1962) and the chemical precipitation of $CaCO_3$ or Fe, Mn, following oxidation (c.f. Bray et al., 1973; Heaney and Davison, 1977).

C. Lake Temperature Estimation

1. Temperature Seiches

After the onset of thermal stratification, we have in the simplest possible case, that the lake's surface is flat calm and the internal isotherms are level. Internal gravipotential energy is then at a minimum. I will call this (rare) situation "isotherm equilibrium". At equilibrium, any point estimate $T(x,y,z,t_o)$ over A_o is an unbiased estimator for $\hat{T}(z,t_o)$ and the total measurement error reduces to the analytical error. "Isotherm equilibrium" represents an end-member situation where all perturbing influences of wind, atmospheric pressure gradients, etc., have receded into the distant past.

In general, temperature is a function of x, y, in addition to z, because of advection of water through open lake systems, and more importantly, because of the immediate and delayed responses of the lake's internal isotherms to the wind "set-up". During period of intense solar radiation and surface warming, the wind transports the warm buoyant lenses of epilimnion surface water to the downwind end of the lake, creating a lateral surface temperature gradient. The stress-dependent lake surface tilting is known as the "set-up" and has amplitude (c.f. Hutchinson, 1957, p. 284):

$$\frac{dh_o}{dx} \doteq \frac{2c_s\ \tau_a}{3g\ \rho_1 \hat{h}_1} \doteq \frac{.67\ \tau_a}{g\ \rho_1 \hat{h}_1} \tag{2}$$

where τ_a is lake surface wind stress (dynes cm^{-2}), g is the gravitational acceleration (980 $cm^2\ s^{-1}$), ρ_1 is the density of the epilimnion (G cm^{-3}), $\hat{h}_1$ is the true mean (over A_o) depth of the mixed layer (cm), and $c_s = 1 + \tau_b/\tau_a$ (τ_b = bottom stress).

Accompanying the "surface seiche" is a large amplitude reverse tilting of the upper pycnocline and the associated upper metalimnion isotherms. Except under conditions of extreme stress, when the tilt of the upper metalimnion isotherms intersects the lake surface (upwelling), the isotherms identified with the bottom of the metalimnion remain more nearly level. The resulting cross sectional view is called the "metalimnion wedge". The relatively small density difference between the epilimnion and hypolimnion (ρ_2-ρ_1) implies that the tilt of the upper pycnocline:

$$\frac{dh_1}{dx} = \frac{2c_s\ \tau_a}{3g(\rho_2 - \rho_1)\hat{h}_1} \sim \frac{.67\ \tau_a}{g(\rho_2 - \rho_1)\hat{h}_1} \tag{3}$$

has an amplitude ~370 times that of the surface tilt for typical summer conditions on Lake Mendota. The linear tilt or "wedge" model is a useful idealized representation of an actual lake's internal response to an imposed wind stress. Pycnocline displacement increases linearly with τ_a, and with distance outward from the tilt axis node. The node is the equilibrium position. The upper pycnocline tilt can have sigmoidal character, and differential bottom effects can lead to asymmetry about the tilt node (c.f. Hutchinson, 1957, p. 344; Dutton and Bryson, 1962). In the event a higher lying "breeze thermocline" develops, the upper thermocline is tilted by the wind stress, while the lower one remains nearly stationary. The tilt amplitude is large because both h_1 and $\rho_2 - \rho_1$ are small in this case (c.f. Figure 23).

Equation 3 shows that at constant stress, the amplitude of tilt (upper pycnocline) is greatest in the late spring, when the thermocline is shallow and the temperature (hence density) difference between epilimnion and hypolimnion is still small (Table 7). During summer, tilt displacements are minimum because of the maximum expected density difference. In the fall, the deep thermocline is furthest removed from the perturbing wind stress. If we consider as well the seasonal variations in over lake wind stress (Stauffer, 1980b), the expected tilt amplitudes are reduced still more for the summer, as compared to the late spring. Midday lake stresses in excess of 1.0 dynes cm^{-2} are unusual during summer and 3-hourly stress estimates exceeding 2.0 dynes cm^{-2} were not observed (Madison, WI) during 10 years of summer record (1966-1975). During the height of summer stratification, the maximum calculated tilt displacements at the ends of the 9.0 km WSW-ENE fetch axis are 1.5 to 2 m (from the nodal plane). During the expected diel stress maximum of 0.8 dynes cm^{-2} (between 1200 and 1500 hrs), we would expect approximately a 190 cm difference in elevation for the end points of the upper pycnocline under the summer conditions specified in Table 7.

Table 7. Calculated Displacements for the Mendota Upper Pycnocline for Representative Conditions of Wind Stress and Stratification.*

Wind Stress (Dynes/cm^2)	Season and Stratification Conditions		
	Late Spring[1]	Mid Summer[2]	Fall[3]
0.4	328	96	228
1.0	820	240	570
2.0	1,640*	480	1,140

* Pycnocline intersects lake surface.

Note: Displacements are calculated for the 9.0 km (WSW-ENE) maximum fetch, and represent the elevation difference (cm) of the pycnocline at the ends of that axis.

Lake stratification conditions:

[1] $T_e = 20°$, $T_h = 10°$, $h_1 = 500$ cm, $\rho_2 - \rho_1 = 0.00150$

[2] $T_e = 25°$, $T_h = 11°$, $h_1 = 1000$ cm, $\rho_2 - \rho_1 = 0.00256$

[3] $T_e = 17°$, $T_h = 12°$, $h_1 = 1500$ cm, $\rho_2 - \rho_1 = 0.00072$

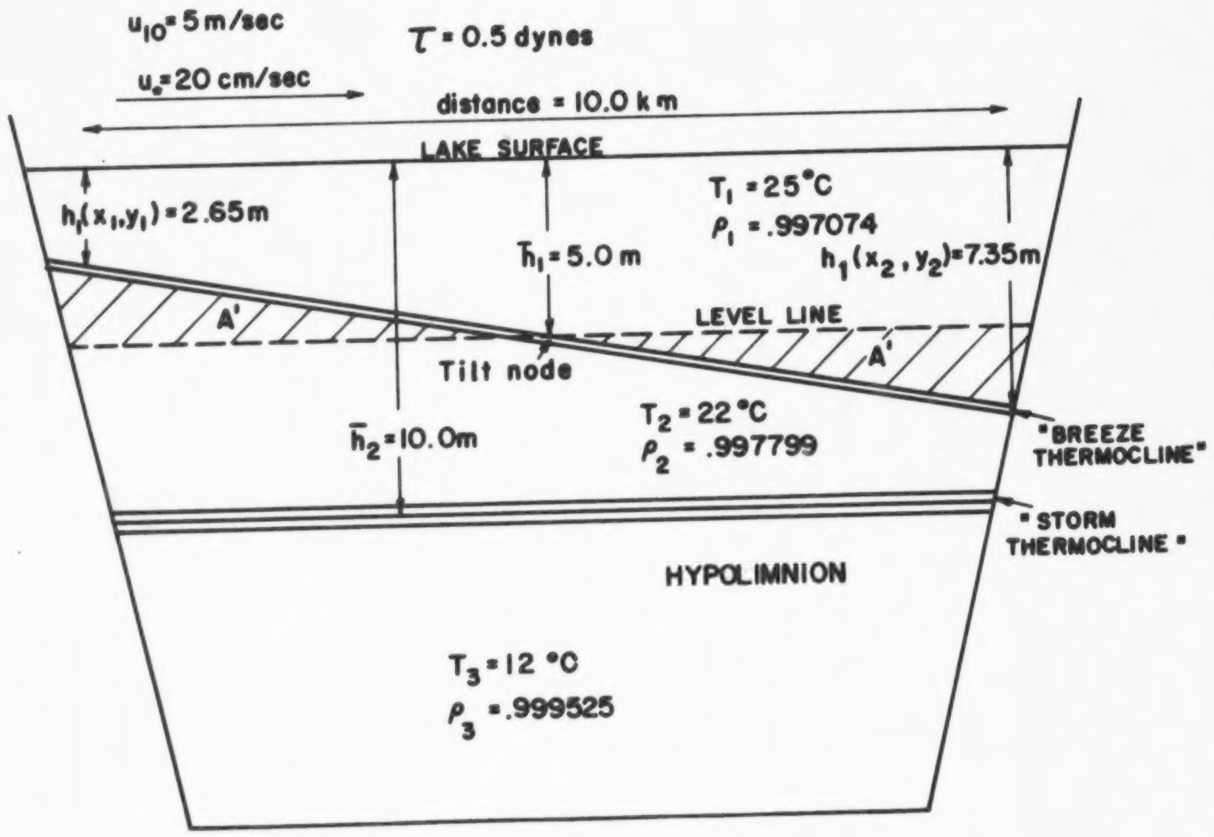
u_{10} = 5 m/sec
τ = 0.5 dynes
u_* = 20 cm/sec
distance = 10.0 km
LAKE SURFACE
$h_1(x_1,y_1)$ = 2.65m
$\bar{h}_1$ = 5.0 m
T_1 = 25°C
ρ_1 = .997074
$h_1(x_2,y_2)$=7.35m
A'
LEVEL LINE
A'
Tilt node
$\bar{h}_2$ = 10.0m
T_2 = 22 °C
ρ_2 = .997799
"BREEZE THERMOCLINE"
"STORM THERMOCLINE"
HYPOLIMNION
T_3 = 12 °C
ρ_3 = .999525

Figure 23. Idealized wind stress tilting of the upper pycnocline.

Removal of the causal wind stress initiates the short period-low amplitude surface seiche and the long period, large amplitude internal (temperature) seiches. For temperature estimation, the surface seiche is of negligible importance. The long period internal waves are very important because of their invisibility to a surface observer, large displacements, and broad spectrum of periodicities.

The periods (P_i) of the internal oscillations based on a two layer model range upward to that observed for the uninodal seiche and can be calculated approximately using Equation 4 (Hutchinson, 1957, p. 336).

$$P_i = \frac{2\ell_f}{i\left\{\frac{g(\rho_2 - \rho_1)}{1/h_2 + 1/h_1}\right\}^{1/2}} \tag{4}$$

where ℓ_f is fetch length (cm) and h_2 here is the mean distance from the pycnocline to the lake bottom. For Mendota the uninodal seiche period during mid summer is 10.5-11 hours (Stewart, 1965). The uninodal seiche has the largest amplitude, contains a disproportionately large fraction of the total internal wave energy, and is the slowest to dissipate its stored energy through viscous dampening (Mortimer, 1953). The relative importance of the uninodal and binodal temperature seiches depends on basin morphometry and the depth of the thermocline (Mortimer, 1953). The uninodal seiche periods are proportional to fetch and are long relative to the time required for sampling a medium sized lake.

2. Seiche Dampening

The rate of dampening of internal seiches has apparently not been extensively studied. Mortimer (1953) found approximately 23% dampening with each cycle of the uninodal seiche in the North Basin of Lake Windermere. The dampening rate increases with decreasing $\bar{z}$ because of the increasing drag of the bottom τ_b. Donelan et al. (1974) note that τ_b is proportional to the mean square bottom current velocity

$$\tau_b = C_b \overline{u_b}^2 \tag{5}$$

Simons (1973) has reported a bottom drag coefficient, $C_b = 2.5*10^{-3}$ for Lake Ontario, for u_b units (cm s^{-1}). Thus, if as a very rough approximation, we assume the r.m.s. bottom current decreases approximately as $1/\bar{z}$ (for A_o constant), τ_b and hence the dampening rate should decrease approximately as $1/\bar{z}^2$. Clearly, we would expect a rapid rate of seiche dampening for Lake Mendota, and a slow rate for Green Lake, Wisconsin.

3. Other Wave Disturbances

In addition to the seiches, very short period temperature fluctuations (time scale 1-15 minutes) are almost invariably superimposed on the longer period temperature oscillations. These "progressive waves" have low spatial coherence. Stewart (1965) investigated them on Lake Mendota and noted periods ranging generally from 1 to 5 minutes.

Surface gravity waves also affect temperature (and solute) sampling by imposing partially periodic and partially random fluctuations in the observer's surface reference position. The amplitude of the effective vertical fluctuations depends both on wave amplitude and the wave dampening efficiency of the sampling boat. Even during windy conditions, and white-capping, much of the periodic component can be "averaged out" during handling of the sampling line leaving a residual error of 10-20 cm. During calm conditions the error is negligible (<1 cm).

4. Effects of Lake Morphometry on Temperature Estimation

For constant stress over the water surface, increasing fetch linearly increases maximum tilt displacement (Equation 3), hence the initial seiche energy-m^2-surface area increases as ℓ_f. For isomorphic lakes ℓ_f increases with $A_o^{\frac{1}{2}}$ and $S^2_{s.r.s}(h_1)$ is proportional to A_o (Stauffer, 1980h). The proportionality holds only at initial time because we would expect faster rates of seiche dampening in the smaller shallower lakes, than in large deep ones [Note: s.r.s. denotes simple random sample; s^2 = sample variance].

The effect of increasing A_o on $S^2_{s.r.s.}(h_1)$ is actually more subtle than indicated above because of the influence of the lake surface on the wind velocity and, thus, surface stress. For small ($A_o \lesssim 1$ km^2) lakes in heavily wooded or hilly environments, the surface stress is drastically reduced by the shelterbelt effect (Henderson-Sellers, 1977). Furthermore, the shorter roughness length for water as compared to adjacent land surfaces (Deacon and Webb, 1962), and the influence of the bulk Richardson number (Rb), ensure that differential accelerations occur over large lakes than smaller ones (Stauffer, 1980b). The ratio of the wind velocity at reference height 10 m over water (u_{10}) to the velocity at an adjacent land station is frequently called the "wind factor" (c.f. Stauffer, 1980b). As the wind stress is roughly proportional to u_{10}^2, the initial $S^2_{s.r.s.}(h_i)$ for two adjacent lakes differ according to the 4th power of the ratio of their wind factors. Two adjacent lakes can have different wind factors because substantial fetch (up to 50 km) is required for the full acceleration to a new steady-state velocity, and because the wind factor increases as R_b decreases. Because large deep lakes have larger heat budgets than small ones, they lag the solar heating cycle more than smaller lakes (Hutchinson, 1957). The extended lag results in an extension of positive Rb values into the mid summer and accounts for the very small wind factors (~1.0) commonly observed over the Great Lakes in July (Richards *et al.*, 1966). Conversely, in the fall, the very great heat storage of the larger lake leads to a prolonged episode of lapse conditions ($Rb<0$) and consequently large wind factors (~2.0) for long fetch lengths. Clearly, for two adjacent lakes with radically different mean depths and fetches, there is a seasonal influence on the ratio of their wind factors. The ratio is likely to be close to 1.0 during the late spring because of the compensating effects of fetch length and Rb values. In the late summer and fall, however, both the increased fetch and the more negative Rb value selectively accelerate the wind over the larger deeper lake.

5. Variance Components of a Simple Random Sample (s.r.s.) for h_1

If the lake surface is sampled for h_1 using simple random sampling (probability proportional to area), then the sample variance $S^2_{s.r.s.}(h_1,t)$ at time t is given approximately by:

$$S^2_{s.r.s.}(h_1,t) = S^2_{l.w.}(h_1,t) + S^2_{s.w.}(h_1,t) + S^2_{g.w.}(h,t) + S^2_{a}(h_1,t) \qquad (6)$$

The error components partition into expected mean squares due to long period temperature seiches, short period internal waves, and surface gravity waves. The last component is a pure analytical measurement error. For a s.r.s. of size n, the expected mean square error is simply S^2/n (Cochran, 1963).

Although unbiased, a simple random sample is extremely *inefficient* statistically because the mean square is concentrated in the first term of the R.H.S. of Equation 6. This partitioning suggests that our considerable knowledge about temperature seiches should be exploited in constructing a stratified or systematic sample. One technique which can be employed on small lakes is to anticipate the "set-up" by conditioning the sampling design on antecedent wind conditions. If the lake is known to be in a state of "set-up" based on observable strong and unidirectional winds prior to, and during sampling, then the reverse thermocline tilt implies that a single station in either the downwind or upwind lake region results in a strongly biased estimate of h_1. If a single sample is to be selected, a station near the lake's midpoint and hence tilt node should be sampled. The bias depends on the station's distance from the tilt node and the amplitude of the tilt. For a symmetric tilt, pairs of stations, each equidistant from the node provide a strong sampling design.

During relatively calm conditions the lake is not set-up, and it will be difficult to predict *a priori* the tilt of the thermocline based on antecedent wind conditions. In general, as the lake's surface area and mean depth increase, the slow dampening rates for past wind disturbances, and the long lags required to achieve new steady-state circulations under a new stress, make it increasingly difficult to anticipate the set-up. Without prior knowledge of the thermocline tilt, any measurement $h_1 (x,y,t)$ is approximately unbiased for $\hat{h}_1$ because the seiches are oscillatory. However, $V\hat{a}r\ h_1 (x,y,t)$ increases with the mean square (over time) amplitude of tilt at (x,y). Because of the salience of the uninodal tilt, the lake's extremities should individually produce estimators $h_1(x,y,t)$ of $\hat{h}_1$ with the largest variance. As in the case of the set-up, the mean of two stations synoptically sampled which are positioned symmetrically about the tilt node, should provide an estimate of $\hat{h}_1$ with a sharply reduced variance. As it is frequently impractical to sample two stations synoptically, the elapsed time between sampling members of station pairs must be kept short, relative to the half period of the uninodal temperature seiche. One of the inherent dangers in transect sampling is that the elapsed time between sampling station pairs near the ends of the transect can easily approach the half-period of the uninodal temperature seiche. Obviously, a pair of sampling boats can be employed to great advantage to make the sampling of individual station pairs nearly synoptic.

6. Bias in $\bar{T}(z)$

The simplest and most commonly employed procedure for estimating the lake-average temperature profile is Equation 7, where n is the number of individual profiles sampled.

$$\bar{T}(z) = \frac{1}{n} \sum_{i=1}^{n} T_i(z) \qquad (7)$$

Sweers (1968) noted that the "average temperature curve", $\bar{T}(z)$ can provide biased estimates of the true "equilibrium" temperatures $(\hat{T}(z))$ under conditions of tilted isotherms. As the temperature profile at isotherm equilibrium is required for calculating eddy diffusivitives, the potential bias in $\bar{T}(z)$ can be an important nuisance. Sweers showed that for two conformal sigmoidal $T(x,y,z)$ curves whose metalimnion midpoint depths (z_m) vary by *a* meters, the statistic $\bar{T}(z)$ is negatively biased for $z_m - a < z < z_m$, positively biased for $z_m < z < z_m + a$, and unbiased at $z = z_m$. The scenario described by Sweers (1968) is only partially relevant because Mortimer has repeatedly emphasized that the development of the metalimnion wedge under wind stress results in nonconformal $T(z)$ profiles over the lake surface. Two $T(z)$ profiles (Figure 24) from the main E-W transect of Green Lake, Wisconsin illustrate the thermocline depression and sharpening, and the isotherm spreading and upwelling on opposite ends of the lake, in response to a powerful June 1972 cold front. The Green Lake profiles conform reasonably well to the idealized linear model of the metalimnion wedge (Figure 23).

The bias in $\bar{T}(z)$ can be estimated as the difference between $\bar{z}(T)^{-1}$ (the inverse) and $\bar{T}(z)$, as $\bar{Z}(t)^{-1}$ is a very nearly unbiased estimator for the equilibrium temperature profile (Sweers, 1968). In contrast to $\bar{T}(z)$, which can be computed directly from the raw $T(z)$ data taken at integral meter depths, the $Z(T)$ vectors are determined either graphically or using interpolating polynomials. Interpolation is difficult to do quickly by computer because of the rapidly changing slopes $T'(z)$ and variable depths of the upper pycnocline (over A_o). Thus, it is a matter of some practical utility to identify the conditions leading to unacceptably large $\bar{T}(z)$ biases.

The bias in $\bar{T}(z)$ clearly depends both on the tilt amplitude, and on the sampling design, i.e., the spatial relationships of the sampling stations to the tilt node.

As shown by Figure 24, high amplitude thermocline tilts can occur during powerful cold fronts in late spring, even on lakes of modest fetch (~10 km). In mid-summer, however, the appreciably greater values in $(\rho_2-\rho_1)$ and h_1, and the lower expected wind power inputs (Stauffer, 1980b) reduce the typical afternoon tilt amplitudes. Under these latter conditions, the biases in $\bar{T}(z)$ are confined to a 2 m depth interval and have expected magnitudes <0.3°C for a 5-station balanced sampling design including the tilt node (assumed to be the lake's midpoint) and the ends of the longitudinal (tilt) and transverse axes (Stauffer, 1980h).

7. Biases in $\Delta\bar{T}(z)$

The difference statistic, $\Delta\bar{T}(z) = \bar{T}(z,t_1)-\bar{T}(z,t_o)$, is used for estimating metalimnion and hypolimnion heat gains over time and in estimating vertical eddy conductivity using the flux-gradient method (Powell and Jassby, 1974; Jassby and Powell, 1975). Potential biases in $\Delta\bar{T}(z)$ are thus of concern. A related statistic is the "mixing ratio" $R(z)$ defined by Equation 8 and used by Stauffer and Lee (1973) for estimating entrainment transport of phosphorus resulting from thermocline migration. If the thermocline has been static over the

$$R(z) = \frac{\Delta\bar{T}(z)}{\left\{\bar{\bar{T}}_e(t_o,t_1) - \bar{T}(z,t_o)\right\}} \qquad (8)$$

time interval (t_1-t_o), and if the mean square thermocline tilts are equal on the two sampling dates, then $\Delta\bar{T}(z)$ is unbiased. However, if $h_1(t_1)>h_1(t_o)$, as happens when a powerful cold front activates entrainment, then the metalimnion temperature changes are in general biased. The sign of the bias function depends on depth and boundary translation; the magnitude of the bias function depends sensitively on the boundary translation and the difference in mean square thermocline tilts for the two sampling dates (Stauffer, 1980h). Statistical biases in $\Delta\bar{T}(z)$ clearly militate against lake sampling during, or immediately following, a powerful wind storm, if the objective is to document the effect of the storm on the equilibrium temperature structure.

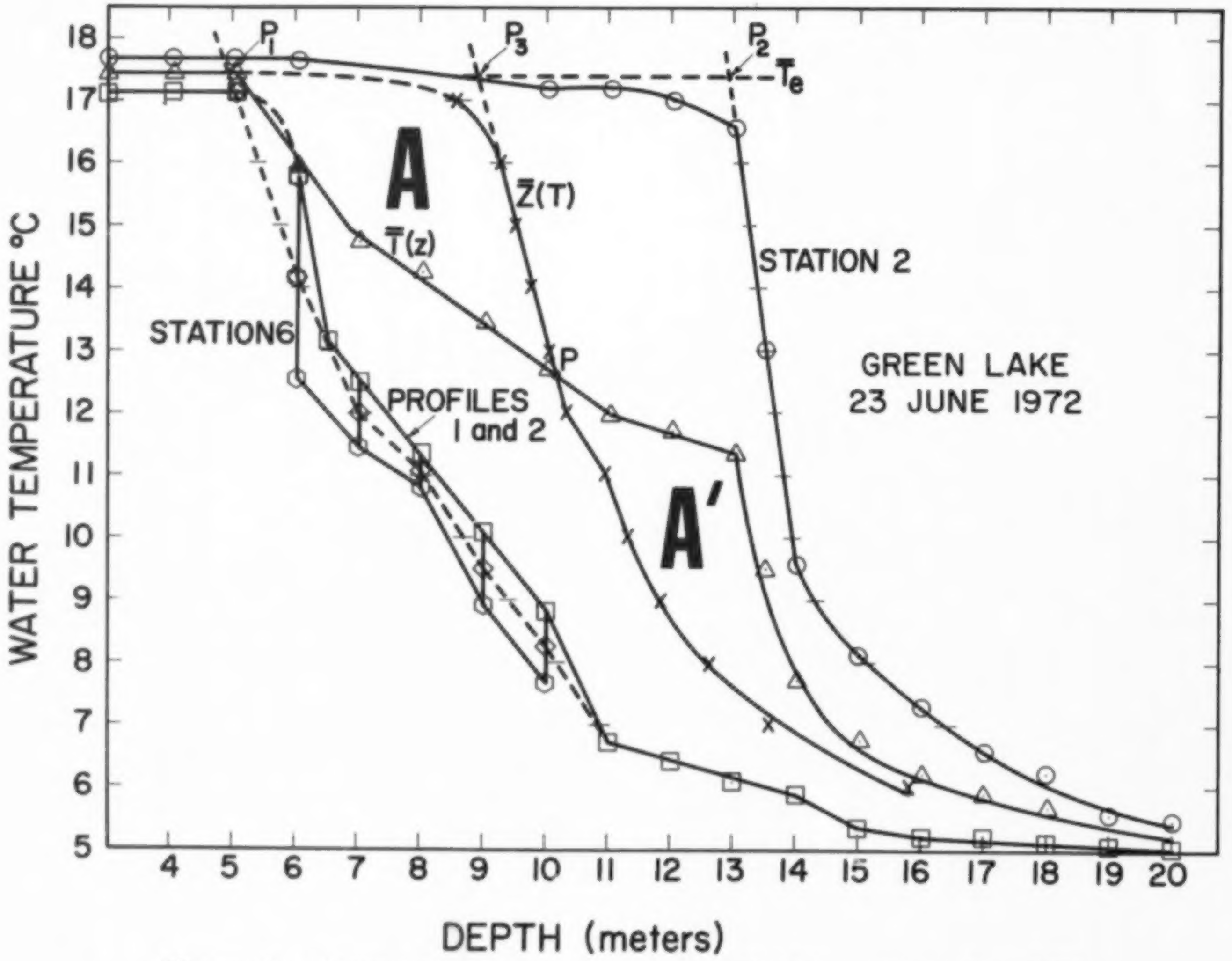

Figure 24. Green Lake thermal structure following a severe June 1972 cold front (Note: Station numbers refer to Figure 17).

D. Estimating Vertical Nutrient Fluxes

The vertical transport of P and/or other dissolved solutes through the thermocline is usually modeled as a "Fickian" eddy diffusion process. The model is generalizable for describing solute transport through any horizontal plane centered j meters below the lake surface.

$$J_s(z) = K_s'(z) * \partial S/\partial z \qquad (9)$$

where $J_s(z)$ is the flux of solute S (units, mg cm^{-2} s^{-1}) through the plane of area A_z centered z meters below the surface; $\partial S/\partial z$ is the solute concentration gradient at level z (units, mg cm^{-4}); and $K_s'(z) = K_s(z) + K_s(z)$ is the effective diffusivity for solute S at level z. Note: $K_s'(z)$ is the sum of the temperature and solute dependent "molecular diffusivity" $K_s(z)$ and the "eddy diffusivity" $K_s(z)$. The eddy diffusivity term depends on turbulent water motions and is considered to be heat or solute independent (i.e., the solutes are passively carried by the fluid). The eddy diffusivity component depends strongly on wind energy inputs to the lake surface and on the local density stabilization of the water column (Stauffer, 1980h; Quay et al., 1980). The molecular diffusivity term is $\sim 10^{-5}$ cm^2 s^{-1} for dissolved ions and two orders of magnitude larger ($\sim 10^{-3}$ cm^2 s^{-1}) for heat (Turner, 1968; Lerman, 1979; Quay et al., 1980). The solute diffusivity increases with temperature and decreases with increasing ion size.

The extreme divergence between the molecular diffusivity rates for heat and solutes causes lake estimation problems if $K_s'(z)$ approaches the molecular rate for heat ($\sim 10^{-3}$ cm^2 s^{-1}). Because heat is used as our conservative tracer for vertical diffusion in lakes (Jassby and Powell, 1975; Quay et al., 1980; Stuaffer, 1980h), $K_t'(z)$ estimated from heat penetration measurements seriously overestimates vertical solute transport if $K_t'(z)$ approaches the molecular value.

In the middle of the summer thermocline of small lakes ($A_o \lesssim 100$ hectares), $K_t'(z)$ approaches the molecular rate (Quay et al., 1980; Stauffer, R. E., unpublished data). In such lakes heat transfer measurements can only be used to define an upper bound on $K_s'(z)$ or 10^{-3} cm^2 s^{-1} within the summer thermocline. This inequality can still be very useful for excluding vertical P fluxes as having importance in these lakes with only modest metalimnion P gradients (Erickson, 1980). If the lake has a small thermocline diffusivity and a very steep P concentration gradient, it will be difficult to resolve the exact magnitude of the vertical flux. In this case a qualified scientific consultant should be hired.

For larger lakes like Mendota or Green, the mid summer thermocline minimum $K_t'(z)$ value averages 1 to $2 * 10^{-2}\ \text{cm}^2\ \text{s}^{-1}$, and increases by at least an order of magnitude during severe storm events (Stauffer, 1980hi; Sweers, 1970). If the lake is shallower and has less density stabilization within the thermocline, the thermocline minimum in $K_t'(z)$ will increase dramatically (Stauffer, 1980h). This holds true for the wind swept western basin of Shawaga Lake and explains the high vertical flux rates of P within that lake (Stauffer and Armstrong, 1980b). In situations where $K_t'(z) >> 10^{-3}\ \text{cm}^2\ \text{s}^{-1}$, the flux of solutes can be computed using the flux gradient model as the product: $K_t'(z) * \partial S/\partial z$.

Stauffer and Lee (1973) introduced a ratio based algorithm for calculating solute transport during storm events. Stauffer (1980h) shows that this "non-Fickian" model is computationally more stable than the flux-gradient algorithm for flux estimates across the important boundary h_1. If the solute behaves essentially conservatively within the upper metalimnion region, the two algorithms yield essentially the same result. If the solute is non-conservative within the upper metalimnion (for example: Fe, or P if the Fe/P ratio is sufficiently large), then the non-Fickian assumptions of the ratio "Mixing Model" lead to larger vertical flux estimates than the flux-gradient algorithm (Stauffer, 1980h).

The calculation of $K_t'(z)$ depends on a number of assumptions. First, we assume that large scale advection of heat and solutes into the hypolimnion-metalimnion from the drainage basin streams is absent. In reservoirs this assumption is frequently invalid. Furthermore, during abnormally wet erosive summer periods, turbid density currents can add heat and solutes to the lake below the boundary h_1 (Bryson and Suomi, 1951). Second, the $K_t'(z)$ calculation algorithm must correct for light penetration and adsorption within the water column and at the sediment water interface (Jassby and Powell, 1975), and also for the penetration of heat *into* the sediments as one component of the hypolimnetic heat storage during stratification (Stauffer, 1980h). Dutton and Bryson (1962) recognized this potential water-sediment heat exchange and proposed that heat transport through the thermocline was largely the result of reversible thermocline temperature seiches in Lake Mendota. Stauffer (1980h) shows that this is *not* an important mechanism for explaining heat fluxes through the Mendota thermocline, or in lakes generally. This possibility was also excluded by Quay *et al*. (1980) for their study lakes in the Experimental Lakes Area of western Ontario, Canada.

The Fortran computer program "LAKETRANS" developed by the author and reported in Stauffer (1980h) can be used for computing thermal diffusivities and solute transport in stratified lakes. The algorithm corrects both for light penetration and sediment heat penetration effects. The sediment-water heat exchange subroutine is based on lake studies by Birge *et al*. (1927) and Likens and Johnson (1969). Vertical solute fluxes are computed both using the flux-gradient model and the reservoir "Mixing Model" reported by Stauffer and Lee (1973).

IV. Chronology of Tasks for Lake Managers

A. Acquire important available data source materials on the lake and its drainage basin.

1. Local Climatological Summaries for the drainage basin (N.O.A.A., U.S. Department of Commerce, Asheville, NC).

    a) Monthly precipitation norms

    b) Monthly mean daily air temperature and humidity

    c) Monthly average wind speeds.

2. Accurate lake bathymetric map (consult state Department of Natural Resources).

3. Lake drainage basin/land use map, including town sites. If this is unavailable, use large scale topographic maps (U.S. Geological Survey) to construct one by drawing in drainage divides.

4. Summary of local hydrologic studies by the U.S. Geological Survey and similar agencies, or private consultants.

    a) Stream gaging

    b) Lake or pan evaporation measurements

    c) Ground water studies

    d) Lake surface level records.

5. Published scientific studies of the lake (usually university based).

B. Determine expected seasonal external nutrient loading (see Reckow, 1980).

1. Estimate the monthly water export from the drainage basin.

2. Based on estimates of lake volume and lake epilimnion volume (see below), estimate the hydraulic "residence" time of the epilimnion.

C. Estimate lake hypsometric relations using the bathymetric map.

1. Convert the bathymetric map to metric units.

2. Determine lake area at each of these bathymetric contour lines. (The easiest and most accurate technique is to cut a map copy along the contour lines and weigh each of these components using an analytical balance.)

3. Interpolate the lake area A(j) at each "integral" meter depth below mean lake surface level.

4. Calculate the sediment contact area, $A_s(j)$, j meters below lake surface, using the central difference formula:

$$A_s(j) = \left(\frac{A(j-1) - A(j+1)}{2}\right)$$

5. Calculate $RA(j) = A_s(j)/A(j)$ for each meter depth. Graph this relationship vs. depth.

D. Determine provisional lake stratification relations.

1. From the climatic norms, dates of ice-on, ice-out [Note: use local sources], and $\bar{z}$ determine the approximate timing and duration of the vernal free convective overturn period.

2. Estimate the "equilibrium surface water temperature", based on mean daily air temperature and relative humidity during the summer "weather stationarity period". Estimate the approximate duration of summer thermal stratification (mixed layer temperature $\geq$ "equilibrium value" - 2°C).

E. Lake physical chemical measurements

1. Estimate lake average concentrations of reactive SiO_2, NO_3-N, NH_3-N, Total-P, and Total Soluble P as soon as possible after ice-out and during the convective circulation period. (Compute the vernal nutrient availability ratio (NO_3-N + NH_3-N):TSP:SiO_2. If the atomic N:P ratio is >14, the lake is likely to be "stoichiometrically phosphate" limited. This will almost certainly happen if the lake is "seepage dominated" in a hydrologic sense.) During the vernal "overturn" period "lake average" concentrations can be estimated by six samples: two samples each at three widely spaced sampling stations "covering" the pelagic zone of the lake. (One sample at each station from near the surface and one from mid water column depth.) Retain several of the vernal overturn samples for major cation-anion analysis.

2. Obtain detailed temperature and solute concentration profiles from the central basin-deep hole sampling station at the following three times:

   a) Soon after (within a week) the lake temperature at 2 m depth in the pelagic region has attained the summer "equilibrium temperature" -2°C.

b) In mid-summer, preferably at the approximate date of hypolimnion onset of anoxia (if this occurs).

c) Near the end of the summer, prior to significant irreversible cooling and thickening of the mixed layer (mixed layer temperature still within 3°C of summer equilibrium value.

3. During the three summer lake surveys collect the following information:

a) Temperature every meter to the bottom.

b) Oxygen every meter from h_1 to the bottom.

c) Total-P. Every other meter except within the main thermocline and in the bottom 4 m of the lake (in the latter two depth zones sample every meter). If the lake is 20 m or less in maximum depth, sample every meter.

d) SiO_2: same as c) above.

e) NH_3-N: same as c) above.

f) NO_3-N: same as c) above until oxygen decreases to below 0.1 mg L^{-1}; then terminate NO_3-N profile.

g) Total Mn: same as c) above.

h) Total Fe: same as c) above.

i) Total soluble Fe: every meter within the bottom 4 meters.

j) Total soluble P: two samples within epilimnion; two samples within the main thermocline; the bottom two samples of the profile.

k) SRP: epilimnion samples.

l) Sulfide: after definite evidence of formation need sample only in late summer within the bottom 4 m to check on FeS solubility control.

m) pH: bottom of hypolimnion if the lake is non-calcareous and the studies are intended to be of scientific interest.

n) Secchi transparency depth.

Note: If the lake has a complicated non-conformal bathymetry, with separate deep holes far removed from the approximate lake center point, and is non-calcareous, a detailed "sampling design" will be required to obtain sufficiently accurate lake-average survey data. Hire a consultant well grounded in both statistical sampling theory and lake hydrodynamics. A consultant should also be retained if the lake surface area exceeds ~50 km^2.

4. Using the analytical results of the three summer lake surveys, and a sophisticated computer program like "LAKETRANS", compute the solute partition by depth, changes in heat and solute storage over time and estimated fluxes among layers of the vertical lake partition. Compute the ratios of Fe:Mn:Tp:NH_3-N:SiO_2 accumulated in the hypolimnion and metalimnion during the two stratification intervals. Note the Fe/P atomic ratio for the bottom of the hypolimnion and within the metalimnion during the two stratification intervals.

5. Resample the lake closely following complete fall turnover. Use the same spatial sampling design specified during the vernal sampling. Compute total lake storage of total P and reactive SiO_2 as the product of lake volume and mean analytical concentration. Compare these mass estimates with the spring and summer sampling periods.

6. Resample the lake at mid depth at several sites immediately after ice-on (few days delay for safety). The concentration of solutes will be the lake-average value prior to the onset of winter stagnation and solute release at the sediment-water interface.

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